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Design calculation for a Wastewater Treatment Plant at a Petroleum Refinery

This project is submitted for the partial fulfillment of

Bachelors of Science B.SC degree in chemical engineering

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شكر وتقدير

الحمد لله الذي لا يبلغ مدحه المادحون ولا يحصى نعمه العادون ولا يؤدي حقه المجتهدون وصلى اللهم على أشرف المرسلين سيدنا وحبيبنا محمد صلى الله عليه وسلم. أود أن أتقدم بجزيل شكري وامتناني الى أسرة قسم الهندسة الكيميائية من أعضاء هيئة تدريس مهندسين وموظفين وفنيين أخص منهم **بالذكر مشرفي وأستاذي الفاضل الدكتور محمد علي البهيليل** لما أبداه من جهود عظيمة وتوجيهات سديدة ومتابعة دقيقة في جميع مراحل هذا البحث توجت بهذه النتائج. واخص بالشكروالتقدير أيضا شركة الزاوية لتكرير النفط من مهندسين وفنيين وعاملين على مساعدتهم وأخيرا لكل من ساندني ولو بكلمة طيبة أقدم لهم شكري وامتناني وتقديري والله الموفق.

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Maram Mohamed Shibani

Dedication

To my mother

To my father

To all my family

To all my friends

To my project supervisor

To the Petroleum Refining Industry

I dedicate this project hoping that someone will get it beneficial and helpful

Maram Mohamed Shibani

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Abstract

This research project outlines an investigation an impact and a method of treatment of liquid wastewater resulting from a Petroleum Refinery (PR) activities. Also, it outlines and determines the sources and the characteristics of the liquid wastewater generated. Through this research work and after the sources of wastewater pollutants were identified, a suitable treatment process technology was implemented in such a way that the impact to the environment is minimized

The Zawiya Petroleum Refinery (ZPR) was visited and considered as a case study area. After the liquid wastewater produced at the Zawiya Petroleum Refinery (ZPR) was identified by its source, characterized by its contaminant type and concentration. This research suggested that the wastewater generated at the Zawiya Petroleum Refinery (ZPR) can be treated successfully through a newly suggested modified plant. Accordingly, the suggested wastewater treatment plant was introduced and design calculations were conducted to each unit. The suggested plant consists of primary treatment that includes: 1-API separator, 2-dissolved air flotation DAF, Secondary treatment (biological treatment) of activated sludge type that includes the following treatment facilities:

1) Bar screen
2) Grit chamber
3) Primary sedimentation tank

4) Aeration tank
5) Secondary sedimentation tank) and
6) Tertiary treatment (nitrification de-nitrification
7) Disinfection by chlorine)
8) Sludge treatment facilities

In this research project, design calculation of each of the above mentioned facilities of the wastewater treatment plant (WWTP) at the refinery is carried out. The WWTP is believed to generate an effluent that is environmentally accepted when compared to the local and international petroleum refinery (PR) effluent wastewater standards. The PR effluent parameters that need to be continuously monitored before releasing to the environment are: pH, BOD_5, COD, Phenolic compounds, sulfides, TSS, total nitrogen (as NH_3-N), oil and grease, nutrients (nitrogen and phosphorus), heavy metals, and microorganisms. The design calculations of the selected units of the petroleum refinery wastewater treatment plant showed good results when compared to other similar plants.

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List of abbreviations

WWTP	Waste Water Treatment Plant
ZPR	Zawiya Petroleum Refinery
(ZORC)	Zawiya Oil Refining Company
PR	Petroleum Refinery
VOC	Volatile Organic compounds
PAC	powder Activated Carbon
API	American Petroleum Institute
CPI	Corrugated Plate Interceptors
DAF	Dissolved Air Floatation
RAS	Return Activated Sludge
W.A.S	Waste Activated Sludge
S.A.S	Surplus Activated Sludge
TOC	Total Organic Carbon
LP	Low Pressure
COD	Chemical Oxygen Demand
BOD	Biochemical Oxygen Demand
IAF	Induced Air Floatation
RBC	Rotating Biological Contactors
AC	Activated Carbon
GAC	Granular Activated Carbon
O&G	Oil and Grease
F/M	Food to Mass Ratio

Chapter one (1)

1. Introduction

What is mint by pollution?

Changes in the physical, chemical and biological characteristics of air land and water that can adversely impact the human and other living species and degradation of the ecosystems the undesirable state of natural environment being contaminated with harmful substance as a consequence of human activities For example: air pollution, soil pollution and water pollution**.**

1.1 Water pollution:

A large amount of water is discharged back to the environment because of its domestic and industrial usage. This type of water is considered contaminated with either organic or inorganic pollutants that vary in toxicity to the environment. This type of wastewater when released to the environment sometimes called domestic wastewater and industrial wastewater effluents. When the concentration of any component in the effluent wastewater far exceed the standard level setup by the local or international environmental authorities, it become essential to treat this effluent. Usually, higher concentration levels can cause pollution, while lower concentration levels can cause contamination that depends of the contaminant that receiving environment .water pollution may be defined as the contamination of streams, lakes, seas, underground water or oceans by substances, which are harmful for living beings. If the concentration of substances naturally present in water increases then also the water is said to be polluted. [1]

1.1.1 Water and wastewater characterization parameters:

Any type of water has its own specifications and characterization. Polluted or contaminated water can be characterized according to the following parameters. Such parameters are used and implemented by the environmental authorities and published in literature .These parameters are explained and listed below:

1-Physical parameters:

The color, odor, turbidity, taste, temperature, pH, total dissolved solids and electrical conductivity constitute the physical parameters and are good indicators of contamination. For instance, color and turbidity are visible evidences of polluted water while an offensive odor bitter and difference than normal taste also makes water unfit for drinking. There are several references that list the various methods and equipment’s used in testing water or wastewater for physical parameters [1].

2- Chemical parameters:

These parameters include the type and concentration of the chemical species or ions present in the water or wastewater. Such as carbonates, sulfates, chlorides, fluorides, nitrates, and metal ions (calcium, magnesium, sodium, potassium). These ions constitute the so called Total dissolved solids (TDS) which is an important water quality parameter in drinking water. Also wastewater can be characterized by the amount and type of organics present. The BOD5 is one indication that used to know the strength of organic waste that can be degraded biologically, COD also a chemical parameter used as indication of the organics present that can be chemically oxidized. There are several references that list the various methods and equipment's used in testing water or wastewater for chemical parameters [1].

3- Biological parameters:

The biological parameters include the type and concentration of microorganisms that might be present in the water .These microorganisms usually like algae, fungi, viruses, protozoa and bacteria. Certain types of microorganisms are considered harmful to the environment and are pathogenic (it can cause illness to humans) when reaches drinking water. Some of them harmful to the aquatic life fish or sea weeds and consumes dissolved oxygen from water. The life forms present in water are affected to a good extent by the presence of pollutants. The pollutants in water may cause a reduction in the population of both lower and higher plant and animal lives. The biological parameters can give indication of the extent amount of pollution in water. There are several references that list the various methods and equipment's used in testing water or wastewater for biological parameters [1].

1.2 Source of water pollution:

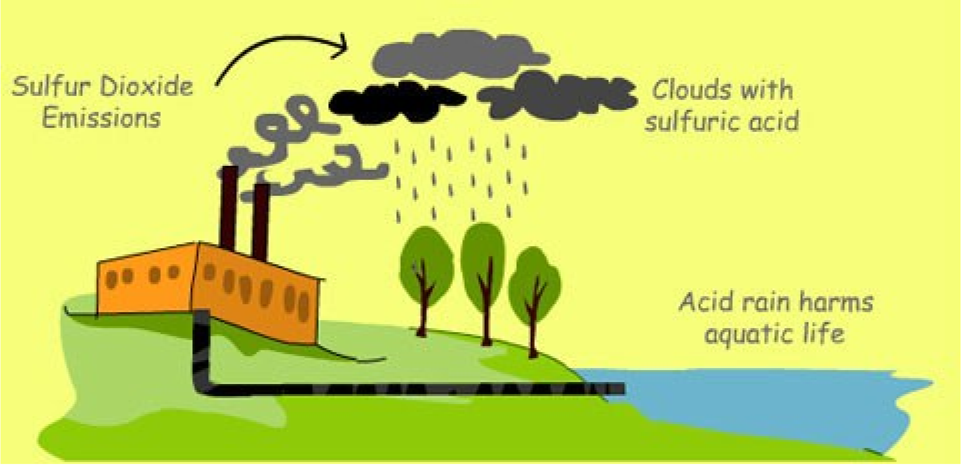
In general, major sources of water pollution is attributed to the following point or nonpoint sources:

1) Sewage pollutants (from domestic or municipal wastewater),
2) Industrial pollutants.
3) Agricultural pollutants.
4) Radioactive and thermal pollutants.

- ❖ Industrial wastewater pollutants

  Several industries cause water pollution from their industrial activities. The major pollutants of industrial source could have different forms such as:

  Sulfur – This is a non-metallic substance that is harmful to marine life.



Asbestos – This pollutant has cancer-causing properties. When inhaled, it can cause illnesses such as asbestosis and some types of cancer.

Lead and Mercury – These are metallic elements and can cause environmental and health problems for humans and animals. It is also poisonous. It is usually very hard to clean it up from the environment once it gets into it because it is non-biodegradable.

Nitrates & Phosphates– These elements are found in fertilizers, and are often washed from the soils to nearby water bodies. They can cause eutrophication, which can be very problematic to marine environments.

Oils – Oils form a thick layer on the water surface because they do not dissolve in water. This can stop marine plants receiving enough light for photosynthesis. It is also harmful to fish and marine birds. A classic example is the British Petroleum (BP) oil spill in the gulf of Mexico 2012 with killed thousands of sea birds and aquatic life species.

- ❖ Oil Pollution by Oil Industries

  Routine shipping, run-offs and dumping of oils on the ocean surfaces happen every day. Oil spills make up about 12% of the oil that enters the ocean. Oil spills cause major problems, and can be extremely harmful to local marine environment, sea birds, sea plants and other aquatic life. Oil with its organic content consumes dissolved oxygen present in the water that is essential for the aquatic creatures to survive. Furthermore, spilled oils are considered non- biodegradable oils. Such oils will take longer periods of time to breakup and dissipate [1].

1.3 Effluent Treatment Plant (ETP)

Effluent treatment plants usually designed and installed before the industry releases its effluent wastewater to the environment. Usually these ETP are designed for treating the effluent industrial wastewater for its reuse or safely disposed to the environment. The ETP involves three important streams namely; influent, effluent and sludge streams and defined as follows:.

a) **Influent**: Untreated industrial wastewater.
b) **Effluent**: Treated industrial wastewater.
c) **Sludge**: Solid part separated from wastewater by ETP.

1.4 Objective of this research project:

The objectives of this work are divided into two categories general and specific objectives:

1.4.1 General objective:

- Select the best treatment alternative that can successfully treat wastewater effluents generated from a crude oil petroleum refinery similar to that at the Zawiya Petroleum Refinery (ZPR).
- Emphasis on impact of effluent Petroleum (PR) wastewater on the Environment sea or land or air.
- Emphasis the methods that can reduce or minimize the impact of effluent Petroleum (PR) wastewater on the Environment. These methods must include: Recycle, Re-use, and Recovery of the wastewater and its contents.
- Emphasize that the implementation of the concept Recycle, Reuse and Recovery will reduce drastically the cost of treatment and reduce the fresh potable water usage and saves energy.
- Emphasize the importance of implementing stringent environmental effluent standards of wastewater generated from a Petroleum Refinery (PR) in protecting the environment from pollution.

1.4.2 Specific objectives:

- Design a wastewater treatment plant suits to that at Zawiya Petroleum Refinery (ZPR).
- The wastewater treatment plant will include design calculation of these facilities: API Separators, Dissolved Air Flotation (DAF), a complete biological treatment system for the removal of organics and total suspended solids, advanced treatment for the removal ammonia nitrogen and disinfection, and finally sludge treatment.
- Compare the calculated design for the above mentioned facilities with the existing at other Petroleum Refinery (PR).

Chapter two (2)

2. Literature review

2.1 Petroleum industry:

The petroleum industry is one of the world's largest industries that involve four major branches:

A. The production branch explores for the acceptance or availability of oil in a certain location, and brings the oil if it is available to the surface and brought for separation facilities and finally stored in specially designed tanks at the oil fields.

B. The transportation branch sends crude oil from storage facilities to the oil terminals for exporting or sent to the oil refineries.

C. The refining branch process crude oil in such a way to extract useful products such as, gasoline, naphtha, diesel oil , and heavy products.

D. The marketing branch sells and distributes the petroleum products to customers. [**2]**

2.1.1 Oil refining:

After crude oil is separated from natural gas at the oil field, it is transported to the refineries and processed to a useful product.

Petroleum refineries are complex facilities specifically designed based on the desired products and the properties of the crude oil feedstock. Refineries may range from medium integrated refineries to fully integrated refineries (or total conversion refineries), based on the application of different processing units.

The refinery feedstock is crude oil, which is a mixture of hydrocarbon compounds. The hydrocarbons in crude oil are a mixture of three chemical groups including paraffin's (normal and iso-paraffins), naphthenes, and aromatics. The most common distinction between crude oil types is 'sweet' or 'sour'. Sweet crude oil is normally low in sulfur content and lightly paraffinic. Sour crude oil is usually high in sulfur content (more than 0.5 wt%) and heavily naphthenic. Crude oils are also classified into light, medium and heavy, dependent on their content of paraffin's, naphthenics, and aromatics.[2]

2.1.2 Petroleum refinery processes:

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas (LPG), gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feed stocks for the petrochemical industry. Typically, petroleum refining activities start with receipt of crude oil for storage at the refinery, include all petroleum handling and refining operations, and they terminate with storage prior to shipping the refined products from the refinery.

The petroleum refining industry employs a wide variety of physical and chemical treatment processes. A refinery processing flow scheme is largely classified by the composition of the crude oil feedstock and the type of final petroleum products required. Typical processing and auxiliary units in refineries are presented below:

1-Separation processes:

Separation process separated crude oil into some of its fraction; Fractional distillation, solvent extraction, and crystallization are some of the major separation process.

a. Atmospheric distillation, **b.** Vacuum distillation, **c.** Light ends recovery (gas processing)

2-Petroleum conversion processes:

Conversion process convert less useful fraction into fractions that are in greater demand cracking and combining processes belong to the class of conversion processes. Cracking processes include thermal cracking and catalytic cracking. These processes convert heavy fractions into lighter ones. During cracking hydrogenation may be used for further increase the yield of the useful products.

Combining processes do the reverse of cracking – they form more complex fractions from simple gaseous hydrocarbons, the major combining process includes polymerization, alkylation and reforming. Other petroleum conversion processes include the following:

a) Cracking (thermal and catalytic),
b) Reforming,
c) Alkylation,
d) Polymerization
e) Isomerization,
f) Coking
g) Vis-breaking.

3-Petroleum treatment processes

The petroleum treatment processes are used to remove impurities from the petroleum fractions. The method of treatment depends on the type of crude oil and on the intended used of petroleum product. Treatment with hydrogen is widely used method of removing sulfur compounds. Other petroleum treatment processes includes the following:

a) Hydro desulfurization,
b) Hydro treating,
c) Chemical sweetening,
d) Acid gas removal
e) De-asphalting.

4-Blending:

Blending with other products or additives may be carried out to achieve certain special properties.

5-Feedstock and product handling:

a. Storage, **b.** Blending, **c.** Loading, d**.** Unloading

6- Auxiliary facilities:

a. Boilers, **b.** Wastewater treatment, **c.** Hydrogen production

d. Sulfur recovery plant

The overall process flow diagram for a generalized crude oil Petroleum Refinery (PR) is presented on figure (2.1)

2.1.3 Petroleum Products:

The products obtained from the crude oil Petroleum Refinery (PR) can conveniently be divided into four groups and as presented below:

- Fuels (Group I):

This group includes liquefied hydrocarbon gases, fuels for carburetor engines (gasoline), fuels for jet (kerosene) and for turbojet engines, diesel fuels, boiler fuels etc.

Liquefied hydrocarbon gases mainly consist of propane and butane along with small quantities of propylene and butylene's.

- Lubricating Oils (Group II):

This group includes various lubricating oils, paraffin's, and petroleum.

- Miscellaneous petroleum products (Group III):

This group includes plastic greases, bitumen's, coke etc.

- Chemical and petrochemical products (Group IV):

This group includes hydrocarbons of various classes which serve as starting products for organic and petrochemical synthesis. [2]

Table (2.1): Processes of petroleum refinery and their products:

Process name	**Action**	**Method**	**Method**	**Feedstock(s)**	**Product(s)**
FRACTIONATION PROCESSES					
Atmospheric distillation	**Separation**	**Thermal**	**Separate fractions**	**Desalted crude oil**	**Gas, gas oil, distillate, Residual**
Vacuum distillation	**Separation**	**Thermal**	**Separate w/o cracking**	**Atmospheric tower Residual**	**Gas oil, lube stock, Residual**
CONVERSION PROCESSED—DECOMPOSITION					
Catalytic cracking	Alteration	Catalytic	Upgrade gasoline	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Coking	Polymerize	Thermal	Convert vacuum residuals	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Hydro-cracking	Hydrogenate	Catalytic	Convert to lighter HC's	Gas oil, cracked oil, residual	Lighter, higher-quality Products
***Hydrogen steam reforming**	**Decompose**	**Thermal/ catalytic**	**Produce hydrogen**	**Desulfurized gas, O2, steam**	**Hydrogen, CO, CO2**
*Steam cracking	Decompose	Thermal	Crack large molecules	Atom tower heavy fuel/ distillate	Cracked naphtha, coke, residual

Vis-breaking	Decompose	Thermal	reduce viscosity	Atmospheric tower residual	Distillate, tar
CONVERSION PROCESSES—UNIFICATION					
Alkylation	Combining	Catalytic	Unite olefins & Iso-paraffins	Tower iso-butane/ cracker olefin	Iso-octane (alkylate)
Grease compounding	Combining	Thermal	Combine soaps & oils	Lube oil, fatty acid, alky metal	Lubricating grease
Polymerizing	Polymerize	Catalytic	Unite 2 or more Olefins	Cracker olefins	High-octane naphtha, petrochemical stocks
CONVERSION PROCESSES--ALTERATION OR REARRANGEMENT					
Catalytic reforming	Alteration/ Dehydration	Catalytic	Upgrade low-octane Naphtha	Coker/ hydro-cracker Naphtha	High octane. Reformate/ Aromatic
Isomerization	Rearrange	Catalytic	Convert straight chain to branch	Butane, pentane, Hexane	Iso-butane/ pentane/ Hexane
TREATMENT PROCESSES					
*Amine treating	Treatment	Absorption	Remove acidic contaminants	Sour gas, HCs w/CO2 & H2S	Acid free gases & liquid HCs
Desalting	Dehydration	Absorption	Remove contaminants	Crude oil	Desalted crude oil
Drying & sweetening	Treatment	Abspt / Thermo	Remove H2O & sulfur Component	Liquid HC, LPG, alky Feed stock	Sweet & dry Hydrocarbons
*Furfural extraction	* Solvent extra .	. Absorption	* Upgrade mid distillate & lubes	Cycle oils & lube feed-stocks	High quality diesel & lube oil
Hydro-	Treatment	Catalytic	Remove	High-sulfur	Desulfurized

desulfurization			sulfur, contaminants	residual/ gas oil	olefins
Hydro-treating	Hydrogenation	Catalytic	Remove impurities, saturate HC's	Residuals, cracked HC's	Cracker feed, distillate, lube
*Phenol extraction	Solvent extra.	Abspt/ Thermo	Improve vis. index, Color	Lube oil base stocks	High quality lube oils
Solvent de-asphalting	Treatment	Absorption	Remove asphalt	Vac. tower residual, Propane	Heavy lube oil, asphalt
Solvent de-waxing	Treatment	Cool/ filter	Remove wax from lube stocks	Vac. tower lube oils	De-waxed lube Base-stock
Solvent extraction	Solvent extra.	Abspt/ Precipetation	Separate un sat. Oils	Gas oil, reformate, Distillate	High-octane gasoline
Sweetening	Treatment	Catalytic	Remove+ H2S, convert Mercaptan	Untreated distillate/gasoline	High-quality distillate/gasoline

2.2 Water pollution by petroleum industry:

The main pollutants from petroleum product are hydrocarbons which due to their inherent properties have the peculiarity of being increasing noxious as they disperse into water.

Although a dense surface discharge may look good it can be easily (except at sea) while paradoxically, a long-standing discharge which has had time to become emulsified is ultimately more harmful oil its removal or treatment is essential. , include both collection system and treatment processes ensuring the finely dispersed hydrocarbons. [3]

2.2.1 Main source of pollution during petroleum industry:-

The pollution sources related to petroleum industry are listed below:

The three source of pollution in petroleum industry originate:

1-At the production:

These are sludge from cuttings and formation water.

2-During transportation:

Let's not mention illicit oil discharges at sea the accidents, usually transportation operation provide tow source of pollution:

I-Ballast water

Ii-Tanker cleaning water

3-During refinery

There are two or three type of effluents:-

(A) Oily water:

Also called rain water from various cleaning operation, from the open cooling circuit and rain falling on:

- Paved area
- Storage retention tanks.
- Loading units

- Pumping facilities.

Recycling the cooling water: whether it be design or required, provides lower volume discharge than open cooling circuit.

Generally, the oily water are polluted by mechanically emulsified effluent and suspended solids; they should not contain sulfides

(B) Storm waters:

In tropical area countries, abundant rainfalls on the above mentioned area sometimes provides 500-3000 m^3/hr flow rate to be treated thus implying a significant –over sizing of the treatment plant.

In temperature countries 20^0C these rainfalls happen rarely and providing (1-8) m^3 of water. This type of water is collected in storm basins and sent to moderately sized treatment line .

(C) Process water:

Different types of wastes are also produced during the refinery operation, which essentially include **gases**, **liquids** and **solids** of varying composition and quantities.

Large volumes of water are employed in refining processes, especially for cooling systems, distillation, hydro-treating, and desalting. Tank drains, equipment flushing, surface water runoff and sanitary wastewaters are also generated. It is therefore clear that refinery wastewater can be broadly categorized as **process** or **non-process** wastewater. In most modern refineries, these different wastewaters are channeled in separate sewer systems.

At least two different independent sewers exist in most petroleum refineries: one that handles storm water and surface runoff and another that handles all process water and water produced from utilities units. However, in most efficient refineries, process water sewers are usually split in more than one sewer depending on the nature of wastewater, thus reducing the load on the wastewater treatment plants, increasing the efficiency of each treatment unit and broadening the possibilities of wastewater reuse in different refining units. Clearly, there is no universal approach to handling and treating refinery wastewater streams.

The quantity of wastewaters generated and their characteristics depend on the process configuration. As a general guide, approximately (3.5–5) m^3 of wastewater per ton of crude are generated when cooling water is recycled. Refineries generate polluted wastewaters, containing biochemical oxygen demand (BOD)and chemical oxygen demand (COD) levels of approximately (150–250) milligrams per liter (mg/l) and (300–600) mg/l, respectively; phenol levels of (20–200) mg/l; oil levels of (100–300) mg/l in desalted water and up to 5,000 mg/l in tank bottoms; benzene levels of 1–100 mg/l; benzene (a) pyrene levels of less than 1 to 100 mg/l; heavy metals levels of (0.1–100) mg/l for chrome and (0.2–10) mg/l for lead; and other pollutants.

Refineries also generate solid wastes and sludge (ranging from 3 to 5 kg per ton of crude processed), 80% of which may be considered hazardous because of the presence of toxic organics and heavy metals

Given the complex and diverse nature of refinery wastewater pollutants, a combination of treatment methods is often the norm before discharge. Therefore separation of wastewater streams, such as storm water, cooling water, process water, sanitary, sewage, etc., is essential for minimizing treatment requirements. [3]

2.2.2 Main wastewater generated from petroleum industry:

Table (2.2) Main wastewater from petroleum industry.

ORIGN	DESIGNATION	VOLUME IN OF CRUDE	HYDROCARBONS COCENTRATION IN WATER	OTHER POLLUTION
Production	Formation water	water 0 TO 6 m^3	500 TO 2000 mg/l	NaCl sand, clay , surfactant
Transportation	Ballast water	25 to30%	Prior to storage after storage average:50-80mg/l paraffin waxes accidentally 500-1000mg/l	NaCl sand, sometimes detergents sulphurous compounds
Refinery	De-salter	5%	50-150mg/l light emulsified hydrocarbons	NaCl possible S--,phenols
	Catalytic cracking	6%	50-100mg/l	S-, RSH,NH3,F-
	Steam cracking		50-100mg/l	phenol ,NH3, S-,oxygen compound

	Rain waters		50-100mg/l	Sand
	De-concentration boilers and coolers		Very low	Salinity phosphates Inhibitors
	Condensates from atoms distillation stripping	2 to2.5%	50-100mg/l	phenol ,NH3
	Condensates from vacuum distillate injector stripping dilution	1 to1.5%	100-150mg/l	phenol ,NH3

2.3 Sources of wastewater generated at the refinery operations:

The type and quantity of wastes produced however, depends mainly upon the following factors:

a) The nature and composition of the crude oil processed and other input materials used in the refining processes.

b) The capacity of the refinery and type of processes employed.

c) Age of the refinery and the production efficiency.

d) Control measure used to reduce the waste generation.

1- Crude oil and product storage:

Crude oil, intermediate and finished products are stored in tanks of varying sizes and specifically manufactured for that particular liquid to be stored in. Wastewater pollutants associated with storage of crude oil and product are mainly oil free, emulsified oil , and suspended solids dispersed in the crude oil .

This wastewater of higher COD levels and to lesser extent BOD levels , and bottom sludge is removed in frequent time intervals. The wastewater generated from leaks, spills, salt filter (used for product drying) and tank cleaning is also removed frequently. Intermediate product storage tanks are frequently considered to be the main source of polysulfide – bearing and iron sulfide suspended solid. Finish product storage tanks can produce higher BOD; alkaline wastewater tank cleaning can contribute to larger amounts of oil, COD, and SS and a minor amount of BOD.

2-Ballast water storage:

Tanks that ship intermediate and final products discharge ballast water. Ballast water have organic contaminations that range from water soluble alcohol to residual fuels brackish water and sediments are also present , contributing high COD and dissolved solids loads to refinery waste water .

3-Crude desalting:

Desalting and dewatering of crude oil upstream of the crude distillation column is a key process operation for the removal of undesirable components from crude oil before it reaches any of the major units.

The continuous wastewater stream from de-salter contains emulsified oil (occasionally free oil) Ammonia, phenol, sulfides and suspended solids all of which produce a relatively high BOD and COD concentration finally, its temperature often exceed 95 °C. This will contribute to the so called thermal pollution when this type of wastewater is released to the environment.

4- Crude oil fractionation:

Fractionation is basic refining process for separating crude petroleum into intermediate fractions of specified boiling point range. The various sub process include pre fractionation, vacuum fractionation and three – stage crude distillation .Wastewater from crude oil fractionation comes from three sources :

The first source is the water drawn off from overhead accumulators prior to recirculation or transfer of hydrocarbons to other fractionators, this source of sulfides and ammonia especially when sour crudes are being processed, it also contains significant amount of oil, chlorides, mercaptan, and phenol.

The second wastewater source is the discharge from oil sampling line, this should be separable, but it may form emulsions in the sewer.

A third waste source is considered very stable oil emulsions formed in the barometric condensers used to create the reduced pressure in the vacuum distillation units. However when barometric condensers are replaced with surface condensers are replaced with surface condenser emulsion do not develop.

5- Thermal cracking:

Thermal cracking can include Vis-breaking and coking, in addition to regular cracking. In each of these operations heavy gas oil fractions are broken down into lower molecular weight fraction such as domestic heating oil, catalytic cracking stock and other fractions by heating. The major source of waste water in thermal cracking is the overhead accumulator on the fractionators, where the water is separated from the hydrocarbons vapor and sent to the sewer system.

This type of wastewater usually contains various amounts oil and fractions and may contain higher levels of BOD, COD ammonia, phenol, sulfides and alkalinity.

6- Catalytic cracking:

Catalytic cracking, like thermal cracking, breaks heavy fractions .The application of a catalyst permits the operations at low temperatures and pressure than with the thermal cracking.

Catalytic cracking units are one of the largest source of sour and phenolic waste water in a refinery .Pollutants come from the steam strippers and overhead accumulators on fractionators, the major pollutants resulting from catalytic cracking operation are oil sulfides, phenols, cyanides, and ammonia. These pollutants produce an alkaline waste water with high BOD and COD concentration sulfide and phenol concentration in the waste water vary with the type crude oil being processed, but at times are significant.

Regeneration of spend catalyst in the steam stripper may produce enough carbon monoxide and fine catalyst particles to constitute an air pollution problem.

7- Hydro-cracking:

This process is basically catalytic cracking in the presence of hydrogen with lower temperatures and higher pressure than FCC. This type of wastewater is probably higher in sulfides and may contain significant quantities of phenol and ammonia.

8- Polymerization:

Polymerization unit convert olefin feed stocks into higher octane polymers polymerization is rather dirty process in terms of pounds of pollutants per barrel of charge. But because of the small polymerization capacity in most refineries the total waste production from the process is small – even though the process makes use of acid catalysts the waste is alkaline because the acid catalysts in most sub process is recycle and any remaining acid is removed by caustic washing .

9- Alkylation:

Alkylation is the reaction of an iso-paraffin and an olefin in the presence of catalyst at carefully controlled temperature and pressure to produce a higher octane alkylate for use as gasoil blending component. Propane and butane are also produced. The major discharges from sulfuric acid , acid alkylation are spent caustics from the neutralization of hydrocarbon stream leaving the alkylation reactor, this waste contain dissolved and suspended solid ,sulfides, oil, and other contaminations but is not major source of waste . Most refineries process the waste sulfuric acid stream from the reactor to recover clean acids, used to neutralize other wastewater streams or sell it as a clean acid. The major source of wastewater materials come from the overhead accumulators.

10- Isomerization:

Isomerization is a process technique for converting light gasoline stocks into their higher octane isomers. No major pollutants discharges problems sulfides and ammonia are not likely to be present in the effluent should also be low in phenolic and oxygen demand.

11- Reforming:

Reforming converts low octane naphtha, heavy gasoline and naphthene rich stocks to high octane gasoline blending stock. Reforming is relatively clean process, the waste water is alkaline and the major pollutants is sulfide from the overhead accumulator on the stripping tower in addition to sulfides it contains small amounts of ammonia mercaptan and oil.

12- Solvent refining:

The major solvent refining processes include solvent de-asphalting, solvent de-waxing; lube oil solvent refining, aromatic extraction, and butadiene extraction. Oil and solvent are the major waste water constituents.

13- Hydro-treating:

Hydro-treating processes are used to saturate olefins and to remove sulfur and nitrogen compounds, odor, color, gum forming materials, and others by catalytic action in the presence of hydrogen, ammonia and sulfides are the primary contaminants, but phenols may also be present if the feed stock boiling range is sufficiently high.

14- Grease manufacturing:

Only small volumes of waste water are discharged from a grease manufacturing process. The largest wastewater loading occurs when the batch units are washed.

15- Asphalt production:

Wastewater from asphalt blowing contains high concentration of oil and has high oxygen demand. Small quantities of phenol may also be present.

16- Drying and sweeting:

It is a broad class of processes used to remove sulfur compounds, water and other. Impurities from gasoline, kerosene, jet fuels, domestic heating oil and other middle distillate products sweetening is the removal of hydrogen sulfide, mercaptans, and thiophenes. Drying is accomplished by salt filters or absorptive day beds. The most common waste stream from drying and sweetening operation is spent caustic, these spent causations have very high in both BOD and COD .

17-Lube oil finishing:

Solvent-refined and de-waxed lube oil stocks can be further refined by clay or acid treatment to remove color-forming and other undesirable materials. Acid treatment produces acid-bearing wastes, the waste stream are also high in dissolved and suspended solid, sulfates, sulfonates and stable oil emulsions. Clay treatment results in only small quantities of waste water being discharged to the sewer. Clay, free oil and emulsified oil are the major waste constituents.

18-Blending and packaging:

Blending is the final step in producing finished petroleum products to meet quality specifications and market demands, this is relatively clean processes. The primary source of waste material is from the washing of rail road tank cars or tankers prior to load finished product, these wash waters are high in emulsified oil.

19-Hydrogen manufacture:

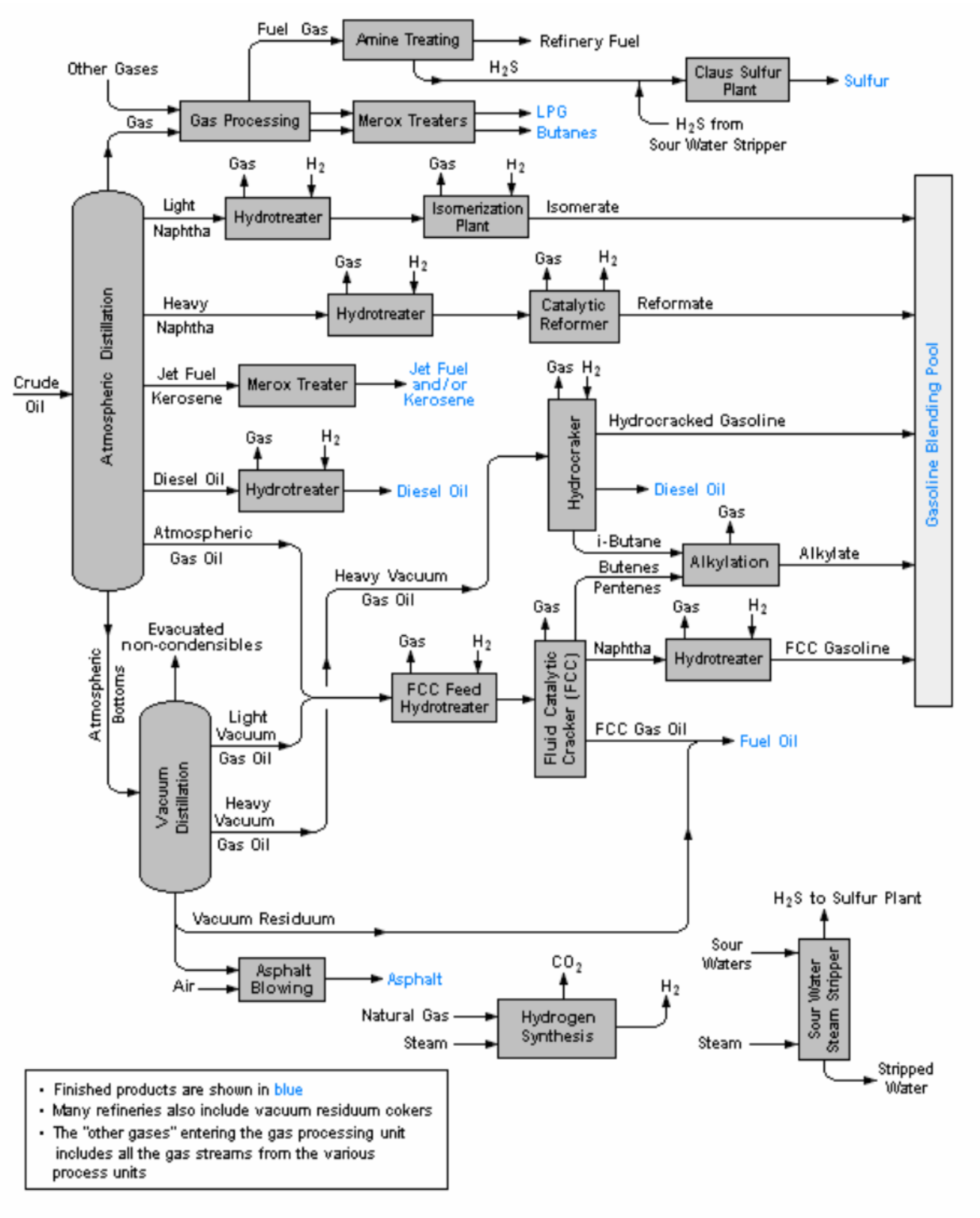
The most widely used process for the manufacture of hydrogen in the refinery is steam reforming. The hydrogen manufacture process is relatively clean a potential waste source is the desulfurization unit. This waste stream contains oil sulfur compounds and phenol.

20-Utility function:

Utility function such as the supply of steam and cooling water generally are set up to service several processes. Wastewater stream from utility functions include boiler and cooling tower blow downs and waste brine and sludge produced by demineralizing and other water treatment systems.

These streams usually contain high dissolved and suspended solids concentration and treatment chemical from boiler and cooling tower, the blow down streams also have elevated temperatures [3].

A typical Petroleum refinery process flow diagram is shown on Figure (2.1) which indicates all operations taking place and the effluent wastewater from particular units.



- Finished products are shown in blue
- Many refineries also include vacuum residuum cokers
- The "other gases" entering the gas processing unit includes all the gas streams from the various process units

Figure (2.1) : Typical process flow diagram of a crude oil Petroleum Refinery

2.3.1 Refinery wastewater:

The source of waste water generation in petroleum refineries discussed previously. [3]

Table (2.3): Qualitative evaluation of wastewater flow and characteristics by fundamental refinery processes:

Production Process	flow	BOD	COD	Phenol	sulfide	Oil	Emulsified oil	pH	Temp	ammonia	chloride	acidity	alkalinity	Suspended Solid
Crude oil and product storage	××	×	×××	×		×××	××	O	O	O		O		××
Crude desalting	××	××	××	×	×××	×	×××	×	×××	××	×××	O	×	×××
									××				×	×
Crude distillation	×××	×	×	××	×××	××	×××	×	××	×××	×	O	××	×
Thermal cracking	×	×	×	×	×	×		××	××	×	×	O	×××	×
Catalytic Cracking	×××	××	××	×××	×××	×	×	×××	××	×××	×	O		×
Hydrocracking	×			××	×××				×	××				××
Polymerization	×	×	×	O	×	×	O	×	×	×	×	×	O	O
Alkylation	××	×	×	O	××	×	O	××	×	×	××	××	O	O
Isomerization	×													
Reforming	×	O	O	×	×	×	O		O	×	O	O	O	O
Solvent Refining	×		×	×	O		×	×	O			O		
Asphalt Blowing	×××	×××	×××	×	O	×××	O							
De waxing	×	×××	×××	×		×								
Hydro Treating	×	×	×		××	O	O	××		××	O	O	×	O
Drying and Sweetening	×××	×××	×	××	O	O	×	××	O	×	O	×	×	××

Where : xxx = major contribution , xx = moderate contribution , x = minor contribution,

O = insignificant , blank = no data

2.4 Wastewater treatment technology:

Conventional refinery wastewater technology is mainly concerned with removing oil, organics, and suspended solids before discharge .However stringent discharge requirements for specific toxic constituents as well as whole –effluent toxicity, specific advanced treatment processes are becoming a necessity for many refineries. Conventional refinery wastewater treatment processes can be categorized into: [5]

Primary, intermediate, secondary and tertiary treatment processes.

1) Primary processes include:

- API separators and parallel or corrugated plate interceptors (CPI) to remove free oil.

2) Intermediate processes include:

- dissolved air floatation (DAF) or induced air flotation (IAF)
- Equalization.

3) Secondary processes include:

Biological treatment in their different forms or combinations, these can include:-

- Activated sludge
- Membrane bioreactor
- Aerated lagoons

- Trickling filters
- Rotating biological contactors(RBC)

4) Tertiary treatment processes include:

- Sand Filtration
- Activated Carbon (AC)
- Chemical oxidation
- Disinfection by chlorine

3-1) Application of biological treatment

Biological treatment processes use natural processes of ubiquitous living organisms during biodegradation, microbial activity ‘recycles’ organic molecules. This continuous process is fundamental to biological treatment. Biological treatment processes are well understood and widely used for organic wastes, but mainly non-hazardous ones. However, they are used for some hazardous organic wastes, particularly those at low hazardous concentrations.

In association with solid waste, biological action takes place naturally within landfill sites and compost processes, and this natural process is encouraged and optimised in biological treatment facilities by control of temperature, nutrient supply and PH.

Different microbial actions take place in aerobic (or oxygen-rich) and anaerobic (or low-oxygen) conditions, the latter being a common way of treating sewage sludge and animal slurries worldwide. Aerobic degradation can take place over wider temperature and moisture ranges than anaerobic processes, because of the methane bacteria.

Aerobic processes may be open or contained, and in-vessel aerobic systems are increasingly being used for solid waste, but anaerobic treatment is typically used for liquid wastes and is carried out in sealed containers or covered lagoons. Many industries with organic waste streams use anaerobic digestion techniques as a pre-treatment stage, to reduce sludge disposal costs (by volatile solids reduction) and to control odours, with – in some cases - the additional benefit of methane collection which can be used to provide on-site energy needs.

3-2) Factors influencing biological treatment

There are a number of factors which influence the choice of biological waste treatment. The suitability of the waste is the most important of those: only organic wastes can be treated. The form of the waste is also relevant: for example, biological processes cannot be used for dry wastes such as dusts, without the addition of moisture to support microbial activity. Wastewater must have a pH within the range pH range [5-10].

A key factor influencing the appropriate choice of a biological treatment method is the capability to ensure good contact between the organic constituents of the waste and the microbial population.

It is almost always possible to find bacteria or other microbes suited to a given waste but these may be specialised bacteria and not one of the ubiquitous kinds, making the containment of the bacteria necessary. For example, it is possible to select a bacterial flora able to live in the effluent from tanneries, which are rich in sulphide and chromium salts, notorious toxics for most bacteria. The specially identified bacteria are able to clean the effluents effectively, something which is impossible for the ubiquitous bacteria. Biological treatment is not suitable for all wastes, only for organic wastes of relatively low toxicity.

The process can never be 100% efficient in destroying organic matter. The number of active bacteria depends on the nutrients, and when the nutrient levels decrease, the bacteria also decrease. As a result, 95% efficiency is generally considered the upper limit for a biological treatment process.

3-3) Process conditions

Biological treatment processes must be conducted within the correct temperature range, with an appropriate moisture level and acidity or alkalinity, and with the right level of aeration.

- Temperature limits – for the appropriate bacteria to live, the temperature must be within the appropriate range. These are usually referred to as mesophilic (30-40^{o}C) and thermophilic (45-55^{o}C) ranges.

- Minimum moisture is always necessary, but other influences, such as aeration, influence the level of moisture needed. For wastewater treatment, which is the most common application for biological treatment, minimum moisture levels are not a concern.
- The capability of the different microbial species to break down organic wastes depends to a large extent on the pH of the medium. Methanogens operate between pH 6 and pH 8. When there is a risk of changes to the acidity, it is advisable to regularly measure and control the PH.
- Aerobic processes can only take place in presence of free oxygen, generally oxygen from the air. For anaerobic breakdown, oxygen is an inhibitor. The most well-known bacteria inhibited by oxygen is the pathogenic agent of tetanus, hence the reason why wounds must always be aerated.
  - Biological processes can be adversely affected by the presence of inhibitors such as metals (copper, silver) or chemicals such as pesticides which may be toxic to the bacteria.

2.4.1 **Primary processes**

Why we need primary treatment

The primary treatment for refinery wastewater is a physical operation, usually gravity separation, to remove the floating and the settle able materials in the wastewater such as suspending solid and organic mater .

In a typical refinery wastewater treatment system, the primary treatment step consists of an oil/water separator where oil, water and solids are separated. This is followed by a secondary oil/water/solids separation step in which a DAF or an IAF unit is used. The primary treatment steps are discussed in detail below. [4]

2.4.1.1Gravity separation oil /water, API separator:

Gravity separators remove a majority of the free oil found in refinery wastewaters. Because of the large amounts of re process able oils which can be recovered in the gravity separators; these units must be considered an integral part of the refinery processing operation and not a waste water treatment process. The functioning of gravity-type separators depends upon the difference in specific gravity of oil and water. The gravity type separator will not separate substances in solution, nor will it break emulsions. The effectiveness of a separator depends upon the temperature of the water, the density and size of the oil globules, and the amounts of characteristics of the suspended matter present in the waste water. The "Susceptibility To Separation" (STS) test is normally used as a guide to determine what portion of the influent to a separator is amenable to gravity separation.

The API separator is the most widely used gravity separator. The basic design is a long rectangular basin, with enough detention time for most of the oil to float to the surface and be removed. Most API separators are divided into more than one bay to maintain laminar flow within the separator, making the separator more effective. API separators are usually equipped with scrapers to move the oil to the downstream end of the separator where the oil is collected in a slotted pipe or on a drum. On their return to the upstream end, the scrapers travel along the bottom moving the solids to a collection trough. Any sludge which settles can be dewatered and either incinerated or disposed of as landfill.

The gravity separator usually consists of a pre-separator (grit chamber) and a main separator, usually rectangular in shape. [4]

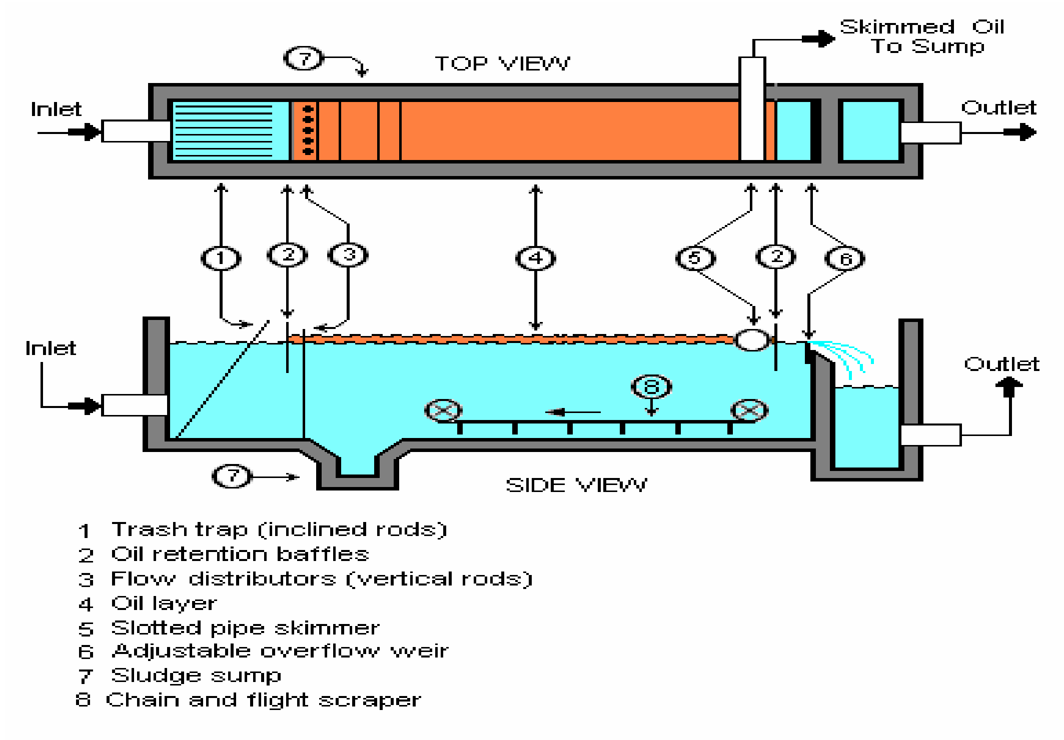


Fig (2.2): API Separator

The gravity separator is usually provided with influent and effluent flow distribution, stilling devices, with oil skimming, and sludge collection equipment. It is essential that the velocity distribution of the approach flow be as uniform as possible before reaching the inlet distribution baffle. Another type of separator finding increasing employment in refineries is the parallel plate separator. The separator chamber is subdivided by parallel plates set at a 45° angle, less than 6 inches apart. This increases the collection area while decreasing the overall size of the unit. As the water flows through the separator the oil droplets coalesce on the underside of the plates and travel upwards where the oil is collected. The parallel plate separator can be used as the primary gravity separator, or following an API separator. [4]

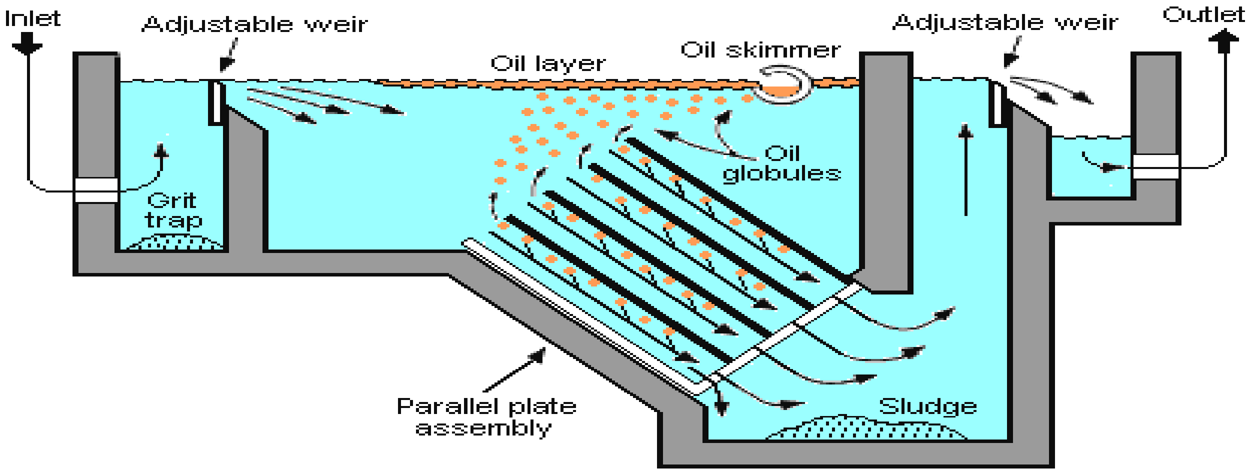


Fig (2.3): Parallel plate separator

If the effluent from the gravity separators is not of sufficient quality to insure effective treatment before entering the biological or physical-chemical treatment system, it must undergo another process to remove oils and solids. Most refineries use either clarifiers, dissolved air flotation units or filters to reduce the oil and solids concentration .Each of these processes has also been used to treat the effluent from a biological system.[4]

2.4.1.2 Gravity clarifiers

Clarifiers use gravitational sedimentation to remove oil and solids from a waste water stream. Often it is necessary to use chemical coagulants such as alum or lime to aid the sedimentation process. These clarifiers are usually equipped with a skimmer to remove any floating oil. Clarifiers used after a biological system normally do not have skimmers as there should be no floating oils at that point. The sludge from the clarifiers is usually treated before final disposal.[4]

2.4.2 Intermediate processes

2.4.2.1 Dissolved air flotation:

Dissolved Air Flotation (DAF) consists of saturating a portion of the waste water feed, or a portion of the feed or recycled effluent from the flotation Unit with air at a pressure of 40 to 60 psig. The waste, water or effluent recycle is held at this pressure for 1-5 minutes in a retention tank and then released at atmospheric pressure to the flotation chamber. The sudden reduction in pressure will result in the release of microscopic air bubbles which will attach themselves to oil and suspended particles in the waste water in the flotation chamber.

This will result in agglomerates which, due to the entrained air, have greatly-increased vertical rise rates of about 0.5 to l.0 feet/minute. The floated materials rise to the surface to form a froth layer. Specially designed flight scrapers or other skimming devices continuously remove the froth. The retention time in the flotation chambers is usually about 10-30 minutes. The effectiveness of dissolved air flotation depends upon the attachment of bubbles to the suspended oil and other particles which are to be removed from the waste stream. The attraction between the air bubble and particle is a result of the particle surface and bubble-size distribution. Chemical flocculating agents, such as salts of iron and aluminum, with or without organic polyelectrolytes, are often helpful in improving the effectiveness of the air flotation process and in obtaining a high degree of clarification. Dissolved air flotation is used by a number of refineries to treat the effluent from the oil separator. Dissolved air flotation using flocculating agents is also used to treat oil emulsions. The froth skimmed from the flotation tank can be combined with other sludge (such as those from a gravity separator) for disposal. The clarified effluent from a flotation unit generally receives further treatment in a biological unit, prior to discharge. [5]

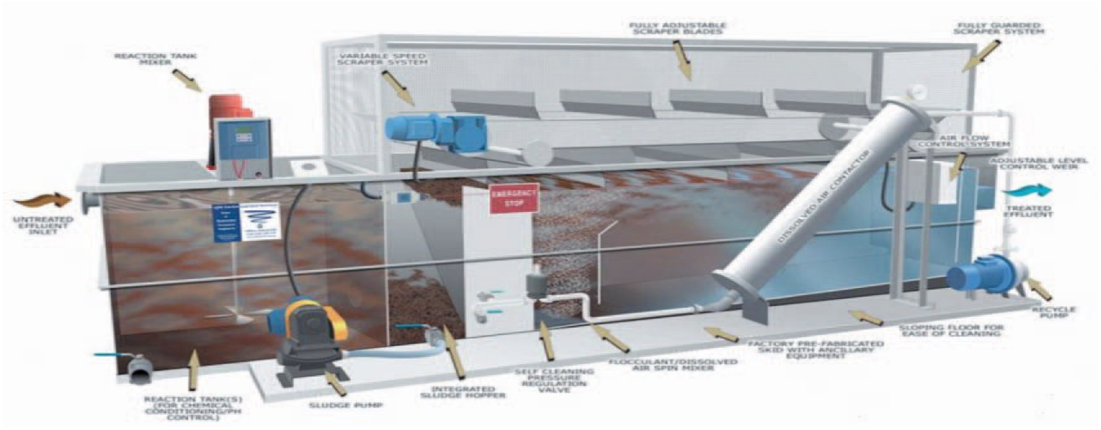


Fig (2.4): Dissolved air flotation

2.4.2.2 Induced air flotation (IAF)

In an IAF unit, air is induced by a rotor-disperser mechanism, the spinning rotor acts as a pump and forces the fluid through the disperser openings and creates a vacuum in the stand pipe. The vacuum in the standpipe pulls the air and mixes it with the liquid. The liquid moves through a series of cells before leaving the unit and the float passes over the weir on one or both sides of the unit. [5]

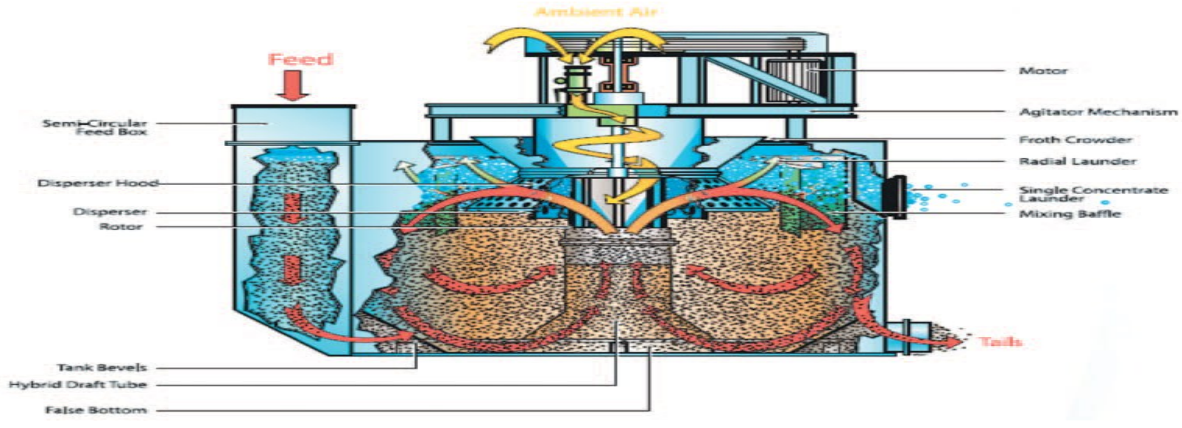


Fig (2.5) : Induced air flotation

2.4.2.3 Equalization

The purpose of equalization is to dampen out surges in flows and loadings. This is especially necessary for a biological treatment plant, as high concentrations of certain materials will upset or completely kill the bacteria in the treatment plant. By evening out the loading on a treatment plant, the equalization step enables the treatment plant to operate more effectively and with fewer maintenance problems. Where equalization is not present, an accident or spill within the refinery can greatly affect the effluent quality or kill the biomass. The equalization step usually consists of a large pond that may contain mixers to provide better mixing of the wastes. In some refineries the equalization is done in a tank. The equalization step can be before or after the gravity separator but is more effective before as it increases the overall efficiency of the separator. However, care must be taken to prevent anaerobic decomposition in the equalization facilities.[5]

2.4.3 Secondary processes

Why secondary treatment (biological treatment) is needed?

Biological treatment is the most widely used wastewater treatment technology for removal of dissolved organic compounds in the oil refining industry. In general, biological treatment can be classified into two categories:

- Suspended growth processes; and
- Attached growth processes.

Suspended growth processes are biological treatment processes in which the microorganisms are thoroughly mixed with the organics in the liquid, and maintained as a suspension in the liquid. Micro-organisms use organic constituents as food for their growth and clump together to form the active biomass. The most commonly practiced suspended growth process used in the treatment of refinery wastewater is the ‘activated sludge processes (discussed below). [5]

2.4.3.1 Activated sludge:

Activated sludge is the most common biological treatment process because of high rate and degree of organic stabilization possible. It is widely used in treating refinery wastewater. Activated sludge is an aerobic biological treatment process in which high concentrations (1500-3000mg/l) of newly grown and recycle microorganisms are suspended uniformly throughout a holding tank to which raw wastewaters are added. Oxygen is introduced by mechanical aerators, diffused air system, or other means. The organic material in the waste are removed by the microbiological growth and stabilized by biochemical synthesis and oxidation reaction. The term activated stems from the fact that the microbial sludge is a floc that is highly active in adsorbing colloidal and suspended waste matter from the aqueous stream.

The basic activated sludge system consists of an aeration tank followed by a sedimentation tank. The microbial floc removed in the sedimentation tank is recycled to the aeration tank to maintain a high concentration of active microorganisms.

The micro-organisms play a major role in converting almost all of the organic matter present in the wastewater in the presence of oxygen. The converted organic matter remains in the system in the form of microbial cells called biomass. The microbial cells or the biomass must be removed from the treated wastewater once reaches a certain time called mean cell residence time (MCRT) before discharge. Thus, final sedimentation tank or the secondary clarifier is often used to remove the settled biomass. Recirculation of biological solids to the aeration tank is important to keep stabilization the system and furthermore serves as a source of viable micro-organisms.

Although refinery wastewater are generally highly amenable to activated sludge treatments, the exact treatability of refinery-petrochemical installation is a function of many factors such as the classification of the refinery, the type of crude charge, the age of the facility and nature of its collection system, the relative effluent volume attributed to utility blow down, and the degree of in-plant control. For these reasons, activated sludge facilities vary from one installation to another. The three basic type of activated sludge system are conventional, contact stabilization and extended aeration system. Other types includes high-purity oxygen system and sequencing batch reactors, but these are not commonly used in refineries.

The conventional activated sludge system allows for absorption, flocculation, and synthesis in a single step. It usually employs long, rectangular aeration tanks that approximate plug flow conditions, or cross flow aeration tanks that approach complete mixing. The oxygen utilization rate is high in the beginning of the aeration tank, but decrease with aeration time or distance down the tank. Where complete treatment is required, the oxygen utilization rate approaches the endogenous value towards the end of the aeration tank. The conventional process can operate over a wide loading range, which is limited by flocculation, settling, and separation requirements of microbial floc.

The contact stabilization system provides for removal of the organic from the wastewater by contact with activated sludge (absorption) and transfer to a separate aeration tank for oxidation and synthesis. This process is applicable to waste containing a large proportion of BOD in suspended or colloidal form. The influent is first contacted wit the activated sludge in an aeration basin for relatively short retention period (15-30minutes). This contact basin removes the suspended or colloidal content from the stream by absorption on the sludge floc. The mixed liquor flows to settler-thickener where the clarified effluent overflows and the thickened sludge flows to stabilization basin. A small part of thickened sludge is discarded as waste. The recycle sludge is aerated in the stabilization basin for 1-5 hours.

During period, the adsorbed organic undergo synthesis and endogenous respiration and the sludge become stabilized. This process results in savings in total basin area as only the recycle sludge, not the whole waste stream, is subjected to long –time aeration.

However, if the oxygen demand of the influent is due to mostly dissolved rather than suspended contaminations, the short retention period in the contact basin may not produce a satisfactory effluent.

The extended aeration system is one in which the synthesized cells undergo auto oxidation resulting in a minimum of solids disposal. Extended aeration is reaction – defined rather than a hydraulically-defined mode and can be designed as a plug flow or a complete mix system. Design parameter include a food/microorganism ratio (F/M) of 0.05-0.15, a sludge age of 15-35 days, and mixed –liquor suspended solids(MLSS) concentration of 3000-5000 mg/l. This process has low cell growth rate, low sludge yields, and high oxygen requirements compared with the conventional activated sludge process. The advantages are high-quality effluent and less sludge production.

The design organic load for most activated sludge systems range from0.1 to 1.0 lb BOD**5**/(day)(lb MLSS). Higher loadings can be imposed, but generally at the expense of poorer efficiency and higher organic levels in the treated effluent. One particularly important parameter for the influent to an activated sludge system in a refinery is oil and grease, which can lower folc density to a level where the sludge – settling properties are destroyed. A study conducted for USEPA indicated that an activated sludge system will perform satisfactory with continuous loading of hexane extractable of 0.1lb/lb MLSS. It was recommended that the influent to the biological system should contain less than 75mg/l hexane extractable and preferably less than 50mg/l .[5]

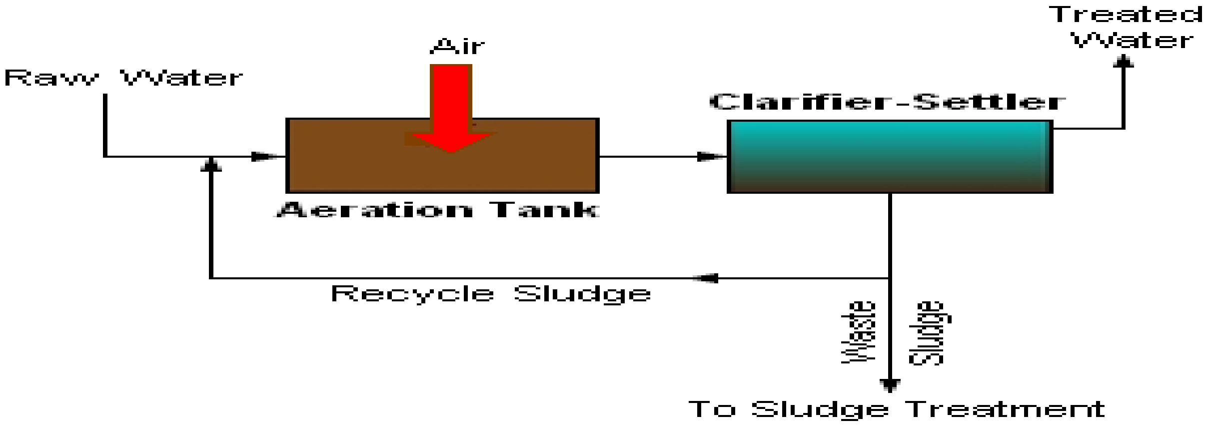


Fig (2.6) :Activated sludge

Purpose:

In a sewage (or industrial wastewater) treatment plant, the activated sludge process can be used for one or several of the following purpose:

- Oxidizing carbonaceous matter: biological matter.
- Oxidizing nitrogenous matter: mainly ammonium and nitrogen in biological materials.

- Removing phosphate.
- Driving off entrained gases carbon dioxide, ammonia, nitrogen, etc.
- Generating a biological floc that is easy to settle.
- Generating a liquor low in dissolved or suspended material.

2.4.3.2 Membrane bioreactor technology

Membrane bioreactors (MBRs) are suspended growth biological treatment processes and are a variation on the activated sludge system. A membrane bioreactor combines a membrane process (e.g. microfiltration) with a suspended growth bioreactor, thereby eliminating the secondary clarification used in an activated sludge system. A schematic of a typical MBR system is shown in Figure.

The micro-filtration membranes are located in a steel membrane tank and are subjected to a low-pressure vacuum that pulls water through the membranes and pumps the filtered water to the next process step while retaining solids in the reactor. Compressed air is injected into the system to scour the exterior of the membranes. The MBR system usually operates at higher MLSS concentrations (15,000–20,000 mg/l) than conventional activated sludge systems. MBR systems are not used in refining due to increased cost compared to conventional activated sludge, however for activated sludge systems that require tertiary filtration, MBR is more cost competitive, since it is equivalent to having an effluent filter. For applications where further tertiary treatment such as reverse osmosis will be used, MBR can be attractive versus the alternative option of using media filtration and microfiltration after biological treatment.[5]

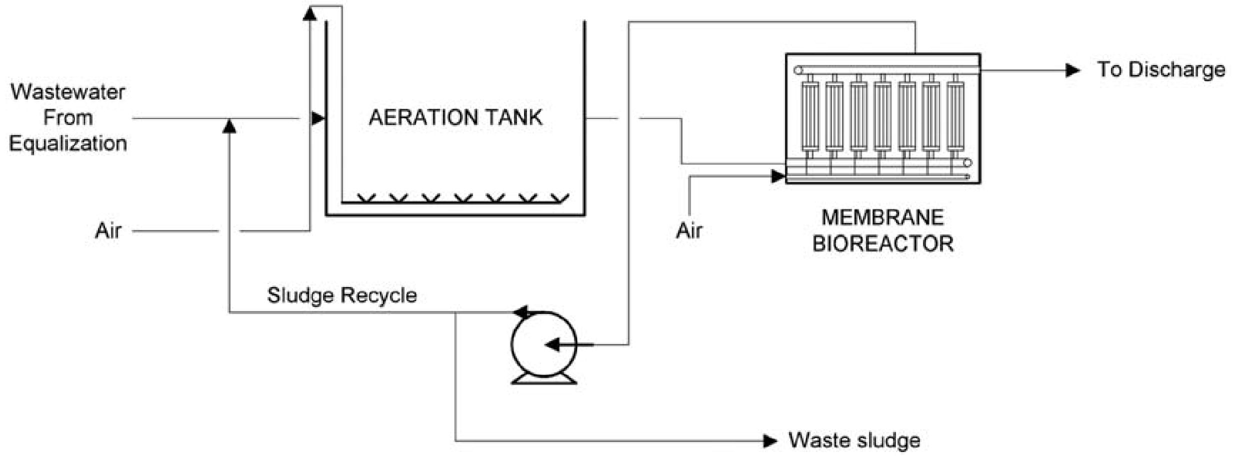


Fig (2.7) : Membrane Bioreactor

2.4.3.3 Aerated Lagoons:

In this type of system, wastewater is treated in a near then in-ground basin that is used for both the aeration and the settling functions. Air is injected through mechanical or diffused aeration units into the lagoon to promote biological treatment. There are usually two types of aerated lagoons:

● Aerobic lagoons**:** In aerobic lagoons, dissolved oxygen is maintained throughout the basins. For this type of a system, settling can take place at a part of the pond separated by baffles or separate sludge settling and disposal facilities might be required. The settled sludge is removed periodically.

- Aerobic-anaerobic/facultative lagoons**:** In these types of lagoons, oxygen is maintained in the upper layer of the liquid in the basin and the rest of the lagoon remains anaerobic. A portion of suspended solids moves to the downstream part of the lagoon where settling takes place and undergoes anaerobic decomposition Aerated lagoons usually require much larger plot areas than other treatment methods, and are commonly employed where land area is not expensive or when discharge standards are not overly restrictive. With the current stringent effluent standards faced by the petroleum industry, aerated lagoons are used less frequently for wastewater treatment in refineries because they cannot produce comparable effluent quality to activated sludge systems.[5]

- Attached growth processes

In attached growth processes, microorganisms are attached to an inert packing material instead of being suspended in the liquid as in suspended growth processes. The packing used in the attached growth processes can be rocks, gravel, plastic material and various synthetic materials. The wastewater comes in contact with the microorganisms that are attached to the media and are converted to more biomass and CO_2. The film of biomass on the media keeps growing and ultimately sloughs off when it reaches a certain thickness. [5]

2.4.3.4 Trickling Filters (TF):

A trickling filter is an aerobic biological process. It differs from other processes in that the biomass is attached to the bed media, which may be rock, slag, or plastic. The trickling filter works according to the following steps:

a) Adsorption of organics by the biological slime.
b) Diffusion of air into the biomass.
c) Oxidation of the dissolved organics.

When the biomass reaches a certain thickness, part of it sloughs off. When the filter is used as the major treatment process, a clarifier is used to remove the sloughed biomass. The trickling filter can be used either as the complete treatment system or as roughing filter. Most applications in the petroleum industry use it as a roughing device to reduce the loading on an activated sludge system.[5]

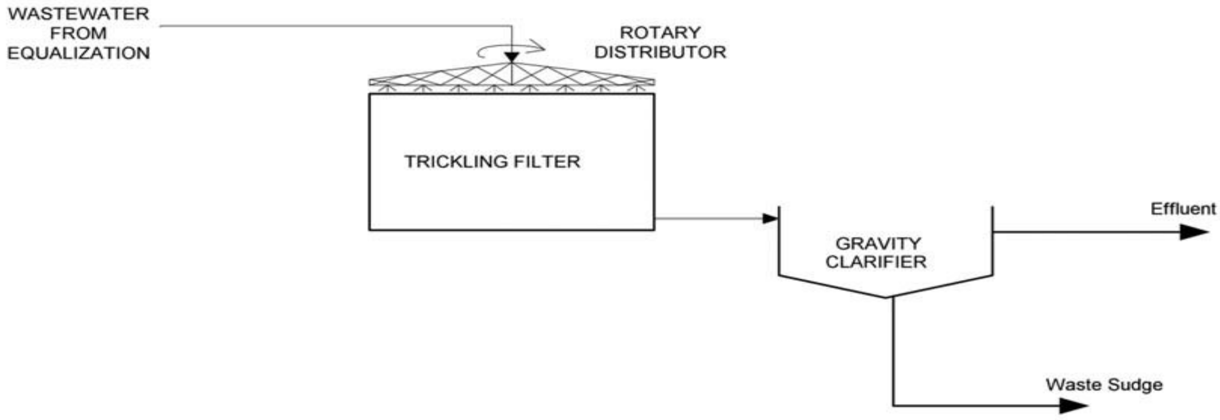


Fig (2.8) : Trickling filter

2.4.3.5 Rotating Biological Contactors (RBC):

The basic element of the rotating biological contactor (RBC) consists of closely spaced plastic discs mounted on a horizontal shaft. The disc material is usually of polystyrene or polyvinyl chloride. These plastic discs are submerged in wastewater and are continuously rotated by the horizontal shaft through an air driven motor. Microorganisms adhere to the plastic surface and form a layer of biological mass (slime) on the discs. Over time, excess sludge is sloughed off the discs.

As the discs are rotating, the attached microorganisms react with the contaminants in the wastewater and convert them to biomass and CO_2. [5] A schematic of a typical RBC system is shown in Figure

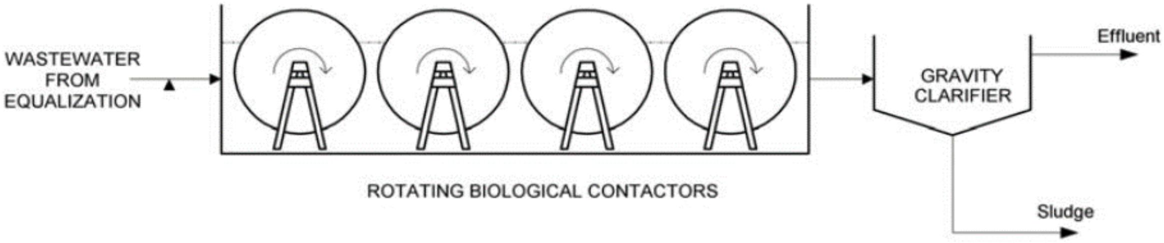


Fig (2.9) : Rotating biological contactor

2.4.3.6 Nitrification or nitrification with de-nitrification

In some cases when a refinery site is required to meet high ammonia or nitrogen limits, the biological treatment system could include either a nitrification (by the use of nitrifying bacteria) or a combined nitrification/de-nitrification step. The level of nitrogen compounds in refinery wastewater can be controlled by avoiding discharges of spent amines and proper removal of ammonia in the sour water stripper. If the concentration of nitrogen compounds is still too high to meet regulatory limits, then nitrification or nitrification/de-nitrification should be included in the biological treatment system. Nitrification is the term used to describe the two-step biological process in which ammonia (NH_4-N) is oxidized to nitrite (NO_2-N) and the nitrite is oxidized to nitrate (NO_3-N). In de-nitrification, the nitrate is reduced to nitric oxide, nitrous oxide and nitrogen gas. Figure (2.10) shows the two arrangements that are used in these systems. In the first system, the aeration/nitrification tank is followed by an anoxic tank where de-nitrification occurs.

A food source (typically methanol) is added to this tank to aid in the process. In the second system, the anoxic tank is followed by the aeration/nitrification tank. In this case, the food source for the anoxic tank is the BOD in the incoming wastewater. A portion of the treated wastewater from the aeration tank is recycled so that the reduction of nitrates in the effluent can occur [5]

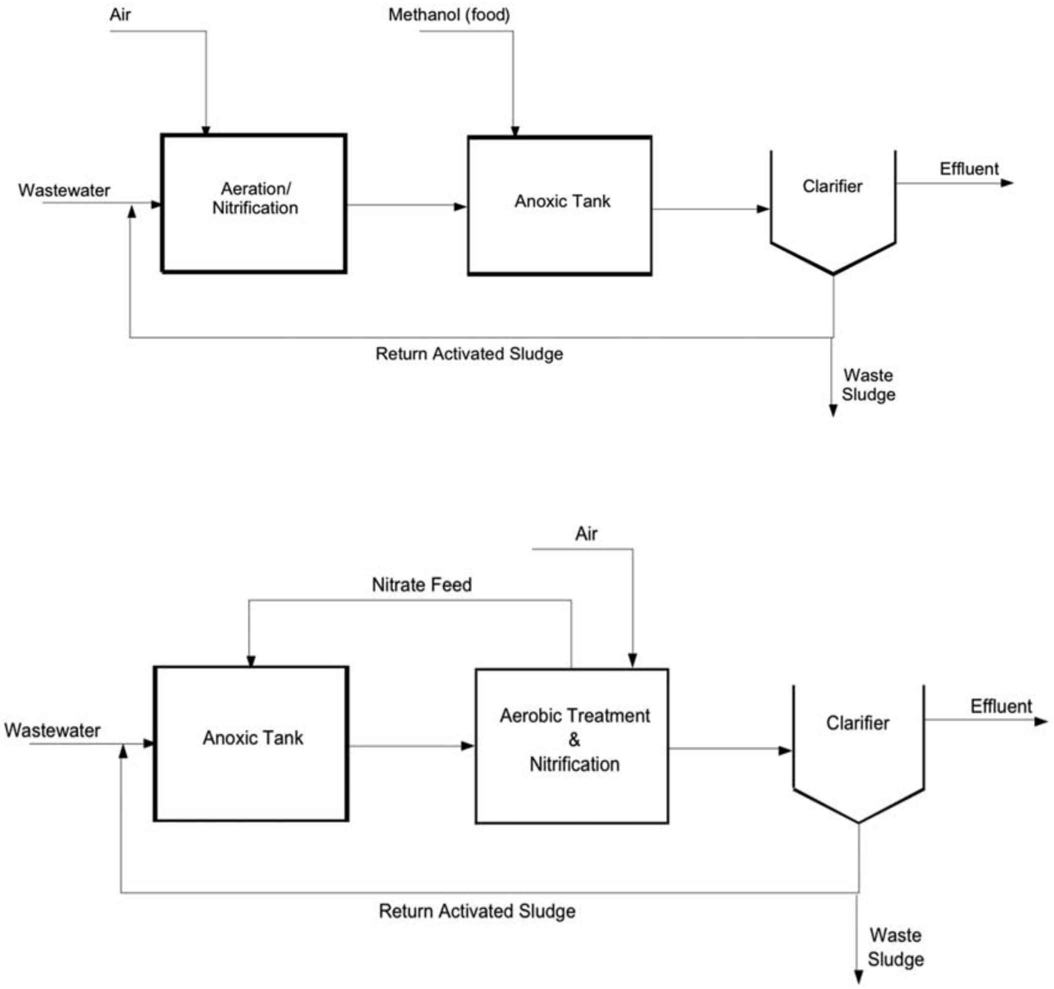


Fig (2.10) : Nitrification/de-nitrification systems

2.4.4 Tertiary processes

Why tertiary treatment is required?

Tertiary treatment is considered to be an advanced treatment process applied in the wastewater treatment plant in order to improve wastewater quality before it is reused, recycled or discharged to the environment.

Tertiary treatment processes may include if necessary these operations and processes such as filtration, activated carbon adsorption, disinfection using ozone, or the application of advanced oxidation processes for the removal of phenol or COD and non- biodegradable organics.

The mechanism of this tertiary treatment involves the removal of the remaining inorganic compounds ,and substances ,such as the nitrogen and phosphorus .Bacteria , viruses and parasites ,which are harmful to public health ,are also removed at this stage Tertiary treatment needs to be considered if the refinery needs to meet stringent limits for the different contaminants represented by the following parameters[5]:

- Total suspended solids (TSS);
- Chemical oxygen demand (COD);
- Dissolved and suspended metals; and
- Trace organics such poly-aromatic hydrocarbons (PAHs)

2.4.4.1 Sand filtration

Effluent from the biological treatment system typically contains about 25 to 80 mg/l of suspended solids depending on the operating conditions in the clarifier. Refineries at many locations need to meet limits as low as 15 mg/l on a consistent basis. In these instances, one option is for the effluent from the clarifier to be filtered using sand filters. This process involves passing the wastewater through a filter bed comprised of a filter media. Dual media filters comprise a layer of anthracite over sand. The larger particles are trapped by the anthracite and the finer solids are held up in the sand. Periodically, the forward flow is stopped and the filter is backwashed to remove the trapped solids. Figure (2-11) shows the typical configuration of a sand filtration system [5].

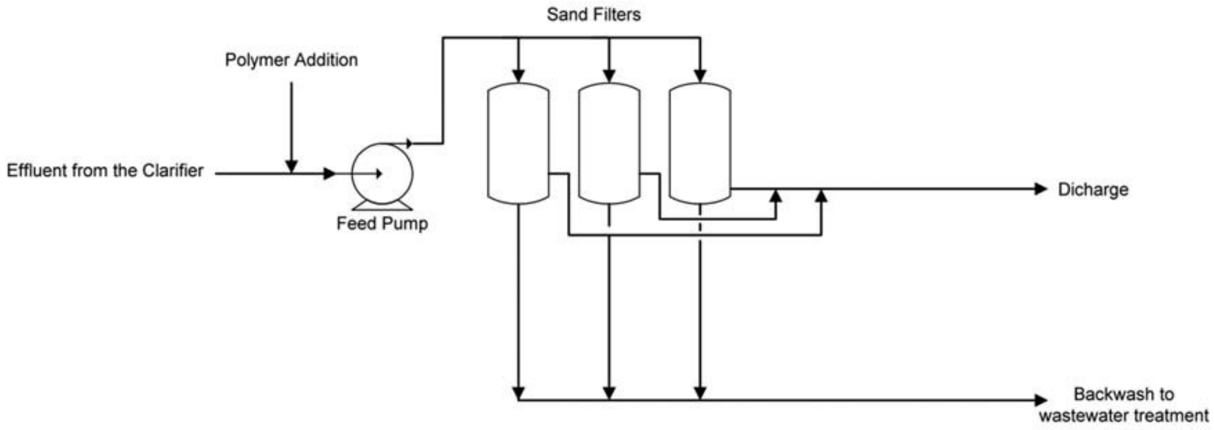


Fig (2.11) : Sand filtration

2.4.4.2 Activated carbon

Removal of dissolved organic constituents from the refinery wastewater can be done by carbon adsorption. In general, activated carbon is usually applied as an effluent ‘polishing’ step (removal of residual organics) for wastewater that has been processed in a biological treatment system. This is because the carbon usage will be prohibitively high if it applied to the refinery wastewater.

In this process the wastewater is passed through a bed of granular activated carbon (GAC) where the organics in the wastewater are adsorbed by the carbon. The carbon bed is periodically regenerated to remove the organics from the exhausted carbon. [5]

Figure (2-12) shows the configuration of a typical carbon adsorption system.

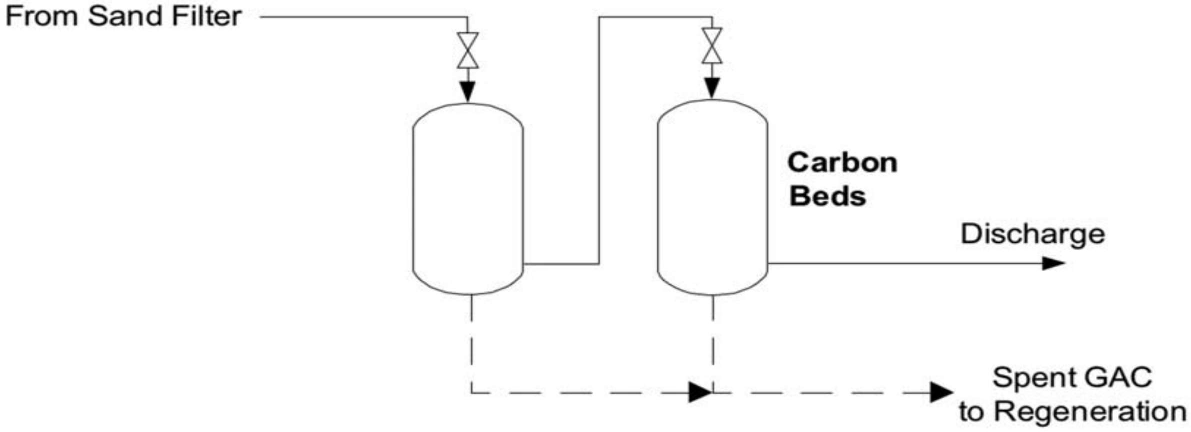


Fig (2.12) : Activated carbon

2.4.4.3 Chemical oxidation

Chemical oxidation in a refinery is generally used for reduction of residual COD, non-biodegradable compounds, and trace organic compounds. It is not common to have a chemical oxidation system in a refinery wastewater treatment plant; details of this approach are included in this document for information purposes.

The following oxidations reagents are very strong oxidants are generally used in a chemical oxidation system as part of the tertiary treatment of water of wastewater:

- Hydrogen peroxide;

- Chlorine dioxide;
- Ozone.

Chemical oxidation can be enhanced in some cases by the use of UV light as a catalyst, but this needs to be evaluated on a case-by-case basis. Figure (2-13) shows the configuration of a typical chemical oxidation system. The feed is sent to the oxidation reactor via a feed tank which provides any surge capacity that is required. Chemical oxidant (hydrogen peroxide, ozone or chlorine dioxide) is prepared fresh to maintain reactivity and fed to the reactor. The effluent from the reactor is then sent to another vessel for adjustment of pH if necessary.[5]

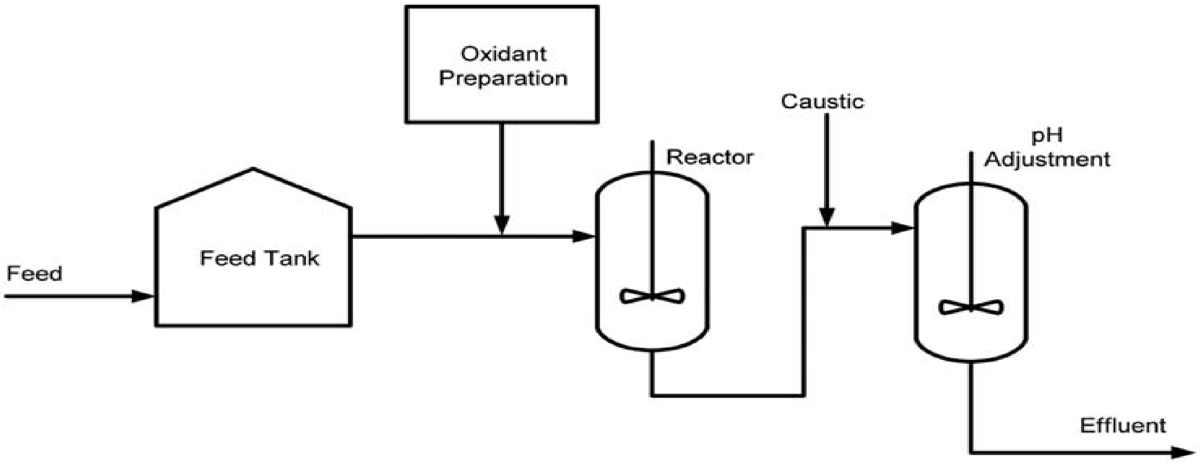


Fig (2.13) : Chemical oxidation

2.4.4.4 Disinfection by chlorine

Chlorine is the most widely used disinfectant agent because it’s effectiveness at lower concentrations, cheaper disinfectant and can form residual if applied in sufficient dosages. The principal **chlorine compounds** used in water and wastewater treatment are:

- Chlorine (Cl_2).
- Sodium hypochlorite (NaOCl).
- Calcium hypochlorite [$Ca(OCl)_2$] ,
- Chlorine dioxide (ClO_2).

Chlorine (Cl_2) can be used in gas or liquid form, the gaseous chlorine (Cl_2) is liquefied at high pressure (5-10 atm) to the liquid form. It is essential to understand the chemistry of chlorine in water before the disinfection process by which the micro-organisms are inactivated.

Chlorine gas reacts readily with water to form hypo-chlorous acid and hydrochloric acid:

$$\mathbf{Cl_2+H_2O \rightarrow HOCl + HCl}$$

The produced hypo-chlorous acid then dissociates to yield hypo-chlorite ions:

$$\mathbf{HOCl \rightarrow H+ + OCl}$$

The relative distribution of HOCl and OCl^- is a function of pH and temperature, Both HOCl and OCl- are excellent disinfectants but HOCl is more effective. Both HOCl & OCl- react with ammonia if exists in water to produce chloramines:

$$\mathbf{NH_3 + HOCl \rightarrow NH2Cl + H_2O\ (Mono\text{-}chloramine)}$$

$$\mathbf{NH_2Cl + 2HOCl \rightarrow NHCl_2 + H_2O\ (Di\text{-}chloramine)}$$

$$\mathbf{NHCl_2 + 3HOCl \rightarrow NCl_3 + H_2O\ (Tri\text{-}chloramine)}$$

Both HOCl & OCl- react with the reducing compounds such as Fe^{+2}, Mn^{+2}, NO^{-2} , and the chlorine will be reduced to the non-effective chloride ion Cl^{-}. Both HOCl & OCl- react with reducing natural organic maters producing Tri-halo-methanes **(THMs) including:**

Chloroform ($CHCl_3$), bromoform ($CHBr_3$) bromo-di-chloro-methane ($CHCl_2Br$), di-bromo-chloro-methane ($CHClBr_2$). The THMs are carcinogenic compounds and their total concentration in drinking water should not be more than 0.1 mg/l. THMs are one of the disinfection by products DBPs that should be minimized or removed before supplying the water to the consumers. Other dangerous DBPs are the halogenated acetic acids HAAs as it may cause cancer. THMs and HAAs can be minimized by removing the organic matter before disinfection. THMs and HAAs can be removed from water by GAC. As illustrated in the previous section; chlorine reacts with the substances existing in water.

When chlorine is added it reacts first with the reducing compounds **such as** Fe^{+2}, Mn^{+2}, NO^{-2}, and the chlorine will be reduced to the none effective chloride ion Cl^{-} When adding more chlorine it will react with NH3 to form chloramines as shown in the chlorine chemistry (from point A to B). When adding more chlorine some chloramines are oxidized to nitrogen gas and the chlorine is reduced to the none effective Cl^{-} ion. (From point B to C).

Continued addition of chlorine will produce free available chlorine (at point C). Point C is called the break point [6]

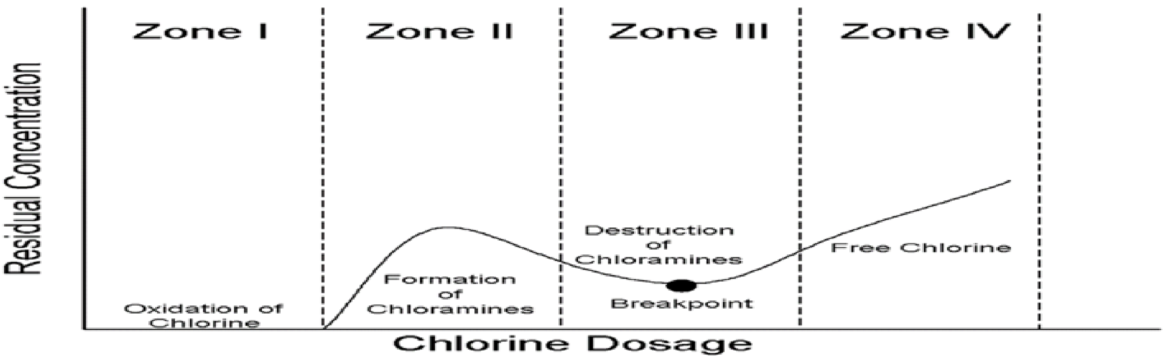


Figure (2-14) Breakpoint chlorination curve

The chlorine added is called the dosage.

The amount used to oxidize the materials existing in water is called the demand.

The chlorine residual = chlorine dosage – chlorine demand

The residual between points A to C is called combined residual because the chlorine is in the form of chloramines. From point C and up, a free chlorine residual starts to appear in water in addition to the combined residual. The free Chlorine residual is composed of un-reacted forms of chlorine HOCl and OCl-. The total residual after the breakpoint equals to the sum of free and combined chlorine. Since the free residual is much more effective in disinfection, all the regulations require a free residual of at least 0.20 mg/l at the farthest tap in the system. The residual chlorine in the produced water is typically (2 – 5) mg/l.

Since free residual chlorine appears only after the breakpoint, the selection of the required chlorine dosage will depend on the breakpoint dosage and calculated according to the equation. [6]

Thus the required dosage = breakpoint dosage + free residual

2.4.2.5 Treatment of sludge's

In a Petroleum Refinery (PR) wastewater treatment plant, sludge is typically generated from the following unit operations:

- Crude oil storage tanks
- API separator—bottom sludge;
- Dissolved gas flotation (DGF) and induced gas
- Flotation (IGF) systems—float and bottom sludge;
- Biological treatment—waste biological sludge.
- API separator—bottom sludge.

The need for treatment of sludge that is removed from the bottom of the API separator depends on refinery configuration as well as local environmental regulations.

This sludge, after further dewatering and de-oiling, can be sent either to off-site disposal or to the coker unit in the refinery (if the refinery has such a process unit). A typical sludge treatment system is shown in Figure (2-15). The API sludge is sent to a decanter tank where water and free oil are removed. If the refinery has a coker unit, the sludge from the tank can be sent to this unit if possible. An alternative is to send it to a centrifuge for further separation. The concentrate from a centrifuge is sent to refinery slops and the sludge sent to off-site disposal. [5]

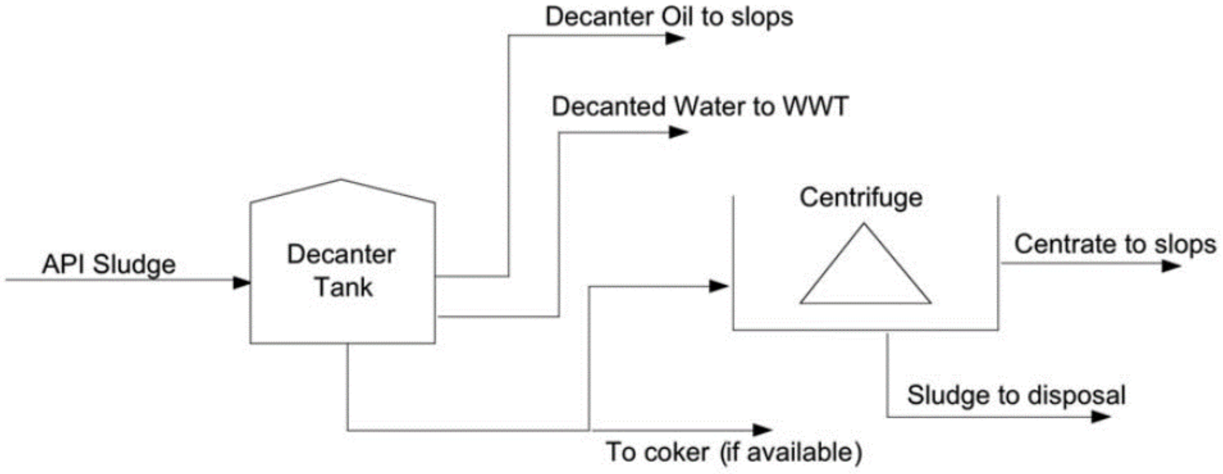


Fig (2.15) API sludge

DGF/IGF float and sludge

The float from the DGF/IAF typically contains emulsions the chemicals (flocculants and coagulants) that are added to aid the separation and therefore require to be handled separately.

Figure (opposite) shows the typical treatment of DGF/IGF float. The float is sent to a tank where emulsion-breaker chemicals are added (if necessary) and the fluid is re-circulated and heated up to break the emulsions. The material in the tank is then sent to disposal.

The sludge from the DGF is normally sent to the same system that treats the API sludge (shown in figure)

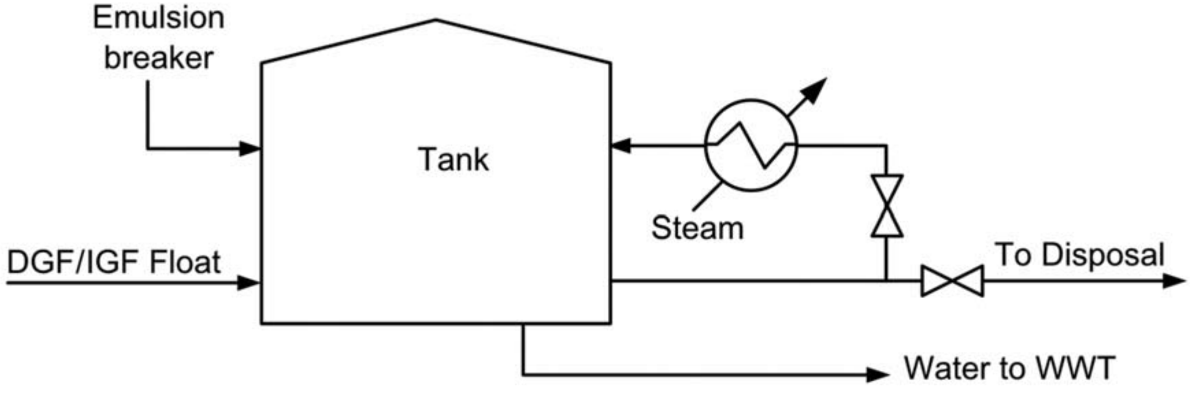


Fig (2.16) : DGF/IGF Float and sludge

Waste biological sludge

Excess sludge that is produced in a biological system can be disposed of (after pretreatment) in several ways, depending on local regulations, including:

- Land farming.
- Landfills.
- Off-site disposal.

The biological sludge is sent to a thickener, which could be gravity or DAF thickener, where water is separated from the sludge and returned to WWT, The sludge from the Thickener is sent to an aerobic digester where air is added to digest the sludge. This step is essentially a volume reduction step to lessen the load on the downstream filter. In some cases the sludge from the thickener is sent to the downstream filter . Several types of filters such as belt filter presses, plate and frame filters can be used. the type of filter that is most appropriate will need to be evaluated on a case-by-case basis.[5]

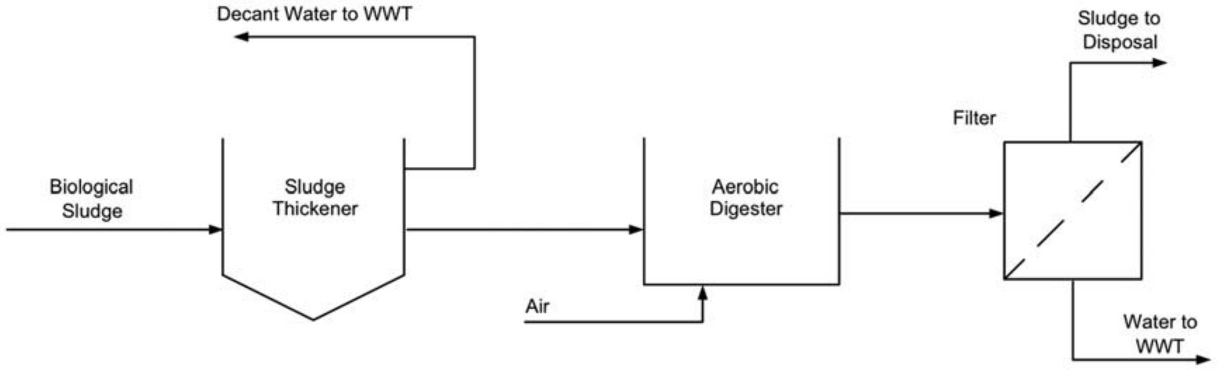


Fig (2.17) : Waste biological sludge

Table (2.4): Common refinery prevention and control techniques

Wastewater Treatment	Oil& Grease	-oil skimming(API separators) -gravity separation(settling tanks and coalescing plate separators) -dissolved/induced air floatation(DAF/IAF) -Biological treatment
	Sulfides	-chemical treatment -clarification
	Organic Compounds	-biological treatment -activated carbon adsorption -clarification
	Metals and Solids	-source reduction --gravity separation(settling tanks and coalescing plate separators) -physical treatment (flocculation) -DAF/IAF -granular media filtration
	Caustics &acids	-neutralization -clarification

Chapter three (3)

Design calculations of the Petroleum Refinery wastewater treatment

3.1 Zawiya Petroleum Refinery (ZPR) :

3.1.1 General:

The Zawiya Refinery is an oil refinery located in Zawiya, Libya, which is about 40 kilometers (25 mi) west of Tripoli the crude came from Saharara field and Hamada field The refinery was founded in 1974 and currently produces an estimated 120,000 barrels (19,000 m^3) of oil products per day (bpd). It is a topping and reforming refinery having a distillation capacity of 6,000 tons per annum. The refinery is operated by the Zawiya Oil Refining Company, a subsidiary of the National Oil Corporation.[1] NOC is expected to re-tender an engineering, procurement and construction contract for upgrading the Zawia refinery This project is aimed at increasing the capacity of the refinery from 120,000 bbl/d (19,000 m^3/d) by 24 percent, which will involve the installation of a new continuous catalytic reformer (CCR) unit, naphtha and gas-oil hydro-treat and an isomerization unit, as well as the installation of pneumatic control units and a supervisory control data acquisition (SCADA) system. The project is being financed by the Libyan government.

Zawiya Oil Refining Company (ZORC) was established under the Libyan National Oil Corporation's Decision, and was given the registration number of 1572 at the Libyan Commercial Register its first

Process Plant was inaugurated, output capacity of 60, 000 BPD of refined oil. In 1977, the second twin Process Plant was added with similar output. In 1980, Zawiya Asphalt Plant was opened, after which Benghazi Asphalt Plant followed in 1984 with an output of 200,000 tons per annum. In 1983, the Lube Oil Plant property was transferred to the Company. This plant produces 60,000 tons per annum of lubricating oils. The main target of establishing the Company was to fulfill the increasing local demand for oil derivatives, besides exporting any surplus products to global markets. In designing this Refinery, international standards were adhered to. Safety and individual, as well as environmental, protection were taken into consideration. Zawiya Oil Refining Company (ZORC) still abides by, and always will, international standards; therefore, it stands on equal footing with other oil refining companies both locally and globally. The Company exercises its utmost to perform its activities in the best manner possible. It also aspires to contribute to the welfare and prosperity of Libya as a whole []

- <u>Main operations (activities) at Zawiya Refinery (ZR):</u>

These include: crude oil refining, asphalt production, blending and filling of mineral oils, besides the exportation of crude oil via its oil harbor, and the importation of oil derivatives needed by the local market. All Company's units and utilities conform with international standards and are provided with the necessary safety and protection facilities as deemed necessary by the nature of its activities.

The main production unit in the (ZRC):

1) Atmospheric Distillation Unit (ADU)
2) Diesel Hydro treating Unit (DHT)
3) Diesel Reforming Unit (DRF)
4) Kerosene Hydro treating Unit (KHT)
5) Liqufied Petroleum Gas (LPG)

- Type of wastewater that entering waste water treatment:

1) Oily water (with flow rate 800 $\frac{m^3}{hr}$)
2) Surface water (with flow rate 800 $\frac{m^3}{hr}$)
3) Rain water (with flow rate 900 $\frac{m^3}{hr}$)
4) Sewage water (with flow rate 50 $\frac{m^3}{hr}$)

Table (3.1): Average oily water flow for waste water entering waste water treatment unit

UNIT	Output (m^3/d)	Composition (fraction)	Oily waste (m^3/hr)
ADU	**19077.9**	**0.245**	**194.75**
DHT	**3240**	**0.1**	**13.5**
DRFF	**1260**	**0.11**	**5.775**
KHT	**3053**	**0.17**	**21.625**
LPG	**141177.495**	**0.09593**	**564.298**
Total	**26630.9**		**800**

Table (3.2): Wastewater influent parameters entering the petroleum refinery treatment unit

Parameter	Unit	Value
Flow rate	m^3/hr	2500
Temperature	°C	20
Oil &grease	mg/l	1500
Phenol	mg/l	10
Ammonia –Nitrogen	mg/l	70
Ferric	mg/l	10
Sulfur	mg/l	5
PH	mg/l	8
TSS	mg/l	3000
TDS	mg/l	2000
BOD	mg/l	200
COD	mg/l	250
Copper	mg/l	1
Magnesium	mg/l	50
Lead	mg/l	0.2
Arsenic	mg/l	0.5

3.2 Design primary treatment

3.2.1-Design API separation

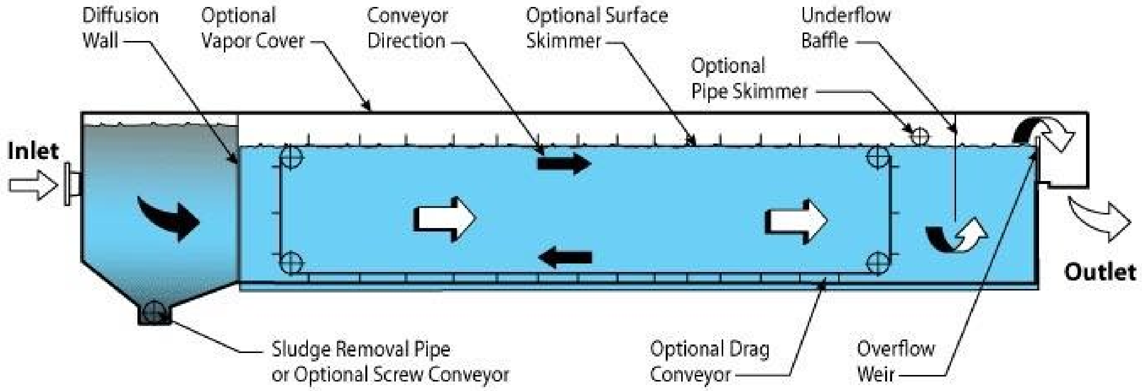


Figure (3 .1): API design

- Design flow rate ($Qd\ = 3522.3 gallon/min$) $= 800m^3\ /hr$
- Two tank contain each tank have ($400m^3/hr$)

A_v =vertical cross section area (d*w)

d = tank depth (1 m<= d <= 2.5 m)

w = tank width (2 m <= w < =5 m)

$V_h = horizontal\ velocity$

Step 1: Trial sizing of oil separator

$try\ \ d = \ 2.5m\ \ and\ \ w = 5m\ \ must\ be(0.3\,w <= \ d <= \ 0.5\,w\ )$

Step 2: Determine horizontal velocity

$$V_h\ \ = \ Q/(d\ *\ w)$$

$$= (\ 400m^3/hr)/(2.5m * 5m)$$

$$V_h\ \ = 32m/hr\ \ \ which\ \ less\ than\ 54m/hr$$

Step 3: Determine rise velocity V_r by using stokes law

$$V_r = 2/9 . R^2 . (\rho_w - \rho_O) * g / \mu$$

$\rho_O = density\ of\ oil$ $(900 kg/m^3)$

$\rho_w = density\ of\ water$ $(1000 kg/m^3)$

$g = gravitational\ acceleration$ $(9.8\ m/s^2)$

$D = the\ droplet\ diameter$ $(150 * 10^{-6}\ m)$

$\mu = viscosity\ of\ water\ at$ $15c0$ $(1.31 * 10^{-3}\ m^2/s)$

$$V_r = \left(\frac{2}{9}\right) * (75 * 10^{-6} m)^2 * \frac{(1000-900)kg}{m^3} * \left(\frac{9.8m^2}{s}\right) / (1.31 * 10^{-3}\ m^2/s)$$

$$V_r = 3.369\ m/hr$$

Step 4: Determine V_h / V_r to check if the assumption is right

V_h / V_r = 32 / 3.369

$= 9.49$ $which\ is\ < 15\ so\ it\ is\ satisfactory$

From the table F =1.5

Step 5: Determine minimum horizontal area of separator A_h

$$A_h = F * Q_d / V_r \quad or \quad Ah = w * I(S)$$

$$= 1.5 * (\frac{400m^3}{hr})/(\frac{3.369m}{hr})$$

$$= 178.09\ m^2$$

Step 6: Determine minimum residence time (t_m)

$$t_m = d / V_r$$

$$= 2.5(m)/3.369(\ m/hr)$$

$$= 0.742\ hr = 44.52min$$

Step 7: Determine minimum length of separator section ($I_{(S)}$)

$$I(S) = F * Q_d * t_m /(w * d) \quad or \quad = F * (V_h/V_r) * d$$

$$I(S) = 1.5 * 400(m^3/hr) * 0.742hr /(5m * 2.5m)$$

$$= 35.61m$$

Step 8: Determine total length ($I_{(t)}$)

$$I(t) = I(f) + I(S) + I(a)$$

$$I(f) = length\ of\ fore\ bay$$

$$I(a) = length\ of\ after\ bay$$

$$I(t) = I(t)/3 + I(s) + I(t)/4$$

$$Where :$$

$$I(s) = 35.61m$$

$Then:$

$$I(t) = 85.46\,m \;\;,\;\; I(f) = 28.488\,m \;,I(a) = 21.365\,m$$

Step 9: Determine minimum hydraulic design volume (V_m)

$$V_m = I(s) * w * d$$

$$= 35.61m * 5m * 2.5m$$

$$= 445.125\,m^3$$

3.2.2- Design dissolved air flotation (DAF):

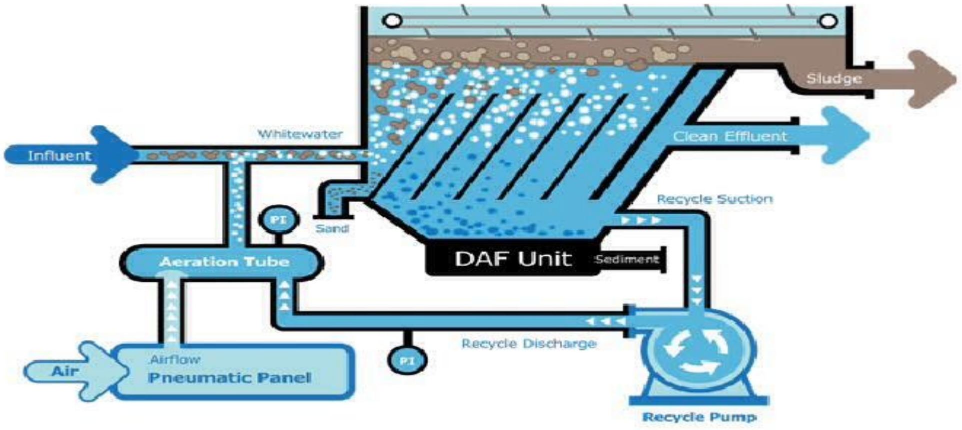


Fig (3.2) : DAF design

- Design flow rate $Q_d = 800\,m^3/hr$
- Recycle pressure p = 3 (atm)
- Recycle temperature T = 20 °C
- Influent TSS = 3000 mg/l
- Dimension of DAF from table: w=7.745 m, L=15.49 m, d=7.745 m

Step 1: Determine surface area A$_d$

$$A_d = w * L$$

$$= 7.745\, m * 15.49\, m$$

$$= 120\, m^2$$

Step 2: Determine the hydraulic loading rate (HLR)

$$HLR = Q_d / A_d$$

$$HLR = 800(m^3/hr)/\, 120m2$$

$$HLR = 6.666\, m/hr \ \ must\ be\ (\ 0.73\ to\ 7.3)m/hr\ so\ it\ satisfactory$$

Step 3: Determine solids loading (SLR)

$$TSS = total\ suspended\ solid\ (3000mg/L)$$

$$S\,L = TSS * Q_d \,/\, A_d$$

$$= 3000\left(\frac{mg}{L}\right) * 1000\left(\frac{L}{m^3}\right) * \frac{1g}{1000mg} * 800(m^3/hr)\ /120m^2$$

$$= 20000g/m^2.hr$$

$$= 4.098\ lb/ft^2.hr\ \ must\ be\ (1\ to\ 6)\ lb/ft^2.hr\ so\ it\ is\ satisfactory$$

Step 4: Determine the quantity of air per quantity of solids (A/S) ratio

$$A/S = 1.3 * as * (f\,P - 1\,)\,/\,TSS$$

$$Where\ :\ \ as:\ air\ solubility = 18.7mg/l\ at\ 20c0$$

$$f\ :\ efficiency\ \ factor\ (0.5)\ in\ temperature\ 20c0$$

$$A/S\ =\ 1.3\ *\ 18.7\ *\ (\ 0.5\ *\ 3(atm) - 1\ )\ /3000(mg/L)$$

$$=\ 0.00405mg\ air\ /\ mg\ solid$$

3.3 Design secondary treatment (biological treatment)

3.3.1Design preliminary treatment (Bar screen)

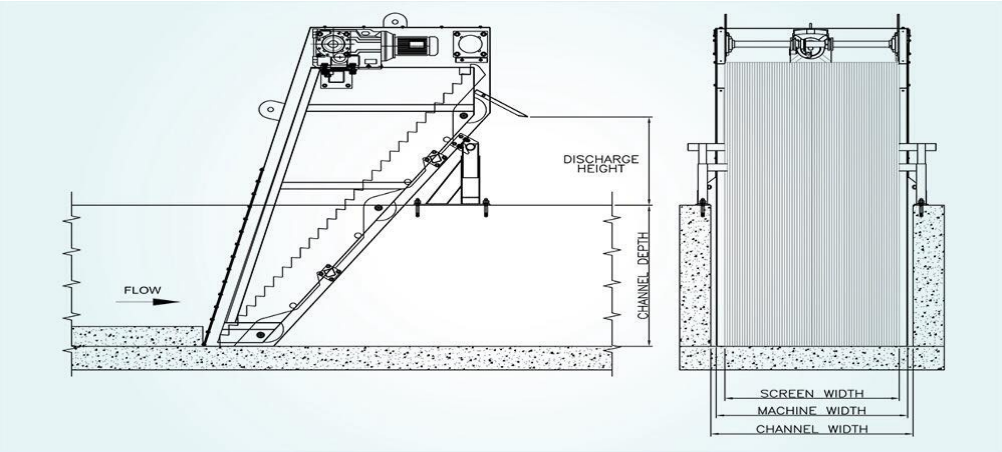


Fig (3.3) : Bar screen design

- $Disgn\ flow\ rate\ Q_d\ = \frac{2500m^3}{hr}\ = \frac{0.694m^3}{s}$
- $V_a = approach\ velocity\ must\ be\ from\ (0.45\ to\ 0.9\ )$
- $m/s\ \ select\ (0.6m/s)$
- $A_C\ =\ cross\ section\ area\ of\ flow\ (m^2)$

Step 1 : Determine $\boldsymbol{the}$ **cross section area of flow A$_c$**

$$A_C\ =\ Q_d\ /\ V_a$$

$$=\ 0.694\ (m^3/s)\ /\ 0.6\ (m/s)$$

$$= 1.157m^2$$

$$A_C = d * w$$

$$d / w = 1.5$$

$$1.157m^2 = w * 1.5\,w$$

$$W = 0.878m \ , d = 1.317m$$

Step 2: Determine cross section area of screen (As)

θ= angle of inclination of the bar

$A_S = A_C / \sin\theta$

$= 1.157 / \sin 50$

$= 1.510m^2$

Step 3: Determine net area of bar screen (A_{net})

$$A_{net} = A_S * \ s / (s + t\ bar)$$

$$t\ bar = thickness\ of\ bar\ screen = (0.02\, m)$$

$$s = space\ between\ bars = (0.03m)$$

$$A_{net} = 1.510\, m^2 * 0.03 / (0.03 + 0.02)$$

$$= 0.906m^2$$

Step 4: Determine velocity through the openings V_b

$$From\ continuity\ equation\ \ V_a * A_C = V_b * A_{net}$$

$$V_b = 0.6(m/s) * 1.157(m^2) / 0.906(m^2)$$

$$= 0.766\, m/s \quad < \quad 0.9\, m/s \quad so\ it\ is\ satisfactory$$

Step 5: Determine head loss (H_{LOSS})

$$H_{LOSS} = (Vb^2 - Va^2) /(2 * g) * (1/ 0.7)$$

$$H_{LOSS} = (0.7662 - 0.62) /(2 * 9.8m/s^2) * (1/0.7)$$

$$= 0.01655m$$

Step 6: Determine number of bar screen (n)

$$n * t\,bar + (n - 1) * s = w$$

$$n * 0.02 + (n - 1) * 0.03 = 0.878$$

$$n = 18.161$$

3.3.2- Design for grit chambers

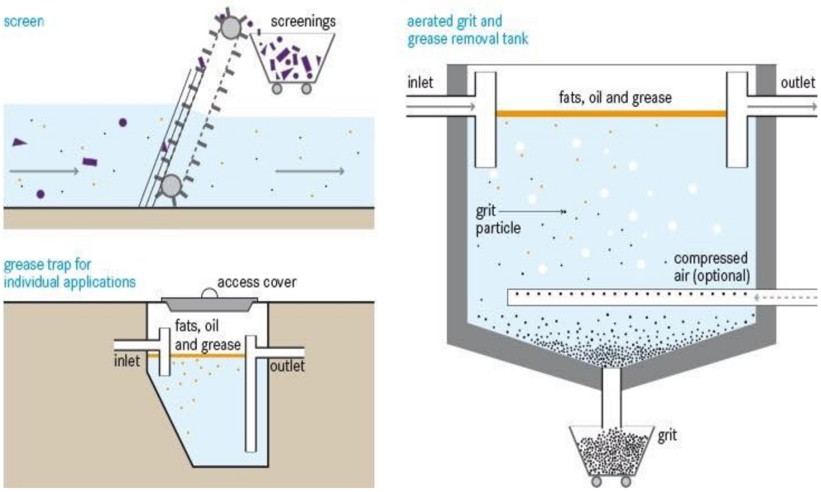


Fig (3.4) : Grit chamber design

- Design flow rate $Q_d = 0.694\ m^3/s$
- Select distention time between (3min to 5min) let t=4min

Step 1 : Determine the volume of grit chamber

$$V = Q * t$$

$$= 0.694(m^3/s) * 4min * 60\ s/min$$

$$= 166.56\ m^3$$

Step 2 : Determine the size of a rectangular chamber

Select the depth = 0.8 + 3 = 3.8m

Step 3 : Determine surface area of chamber A

$$A = volume\ / depth$$

$$= 166.56\ m^3 / 3.8\ m$$

$$= 43.83\ m^2$$

Step 4 : Determine the length of chamber

$$L / w = 4 / 1$$

$$A = w * L$$

$$43.83\ m^2 = w * 4w$$

$$w = 3.310\ m$$

$$L = 13.241\ m$$

Step 5 : Check if the assumption is correct

$$W\ /\ d\ =\ 3.310\ /\ 3.8\ =\ 0.871 \qquad which\ is\ \ (<=\ 1)$$

$$L\ \ /\ d\ \ =\ 13.241/\ 3.8\ =\ 3.484 \quad which\ is(\ \ 3 <\ L/d\ <\ 5)$$

$$So \qquad\qquad w\ \ =\ \ 3.31m\ \ ,\ \ d\ \ =\ 3.8m\ \ ,\ L\ =\ \ 13.241m$$

Step 6 : Determine settling velocity of particle V_s

Assume we have organic mater (S.G = 1.2 , d = 0.1mm)

Assume we have sand mater (S.G = 2.65 , d = 0.2mm)

$$Vfor\ organic\ \ =\ (4\ *\ g\ *\ \ (ps - p)\ *d/(\ 3\ *Cd\ *\ p))^\wedge(\frac{1}{2})$$

$$=\ (4\ *\ 9.8m/s^2\ *\ (1200 -\ 1000\ )Kg/m^3$$

$$(* (1 * 10^{-4})m/\ (3 * 10 * 1000kg/m^3))^\wedge(\frac{1}{2})$$

$$=\ 5.11 * 10 - 3m/s\ = 18.398m/hr\ < 25m/hr\ so\ it\ is\ right$$

$$Vfor\ sand\ \ =\ (\ 4\ * \frac{9.8m}{s^2} * \frac{(2650-1000)kg}{m^3} * 2 * 10^{-4} * (3 * 10 * \frac{1000kg}{m^3})^\wedge(\frac{1}{2})$$

$$= 0.0204m/s\ =\ 73.44m/hr\ <\ 74m/hr\ so\ it\ is\ right$$

3.3.3 Design primary clarifiers

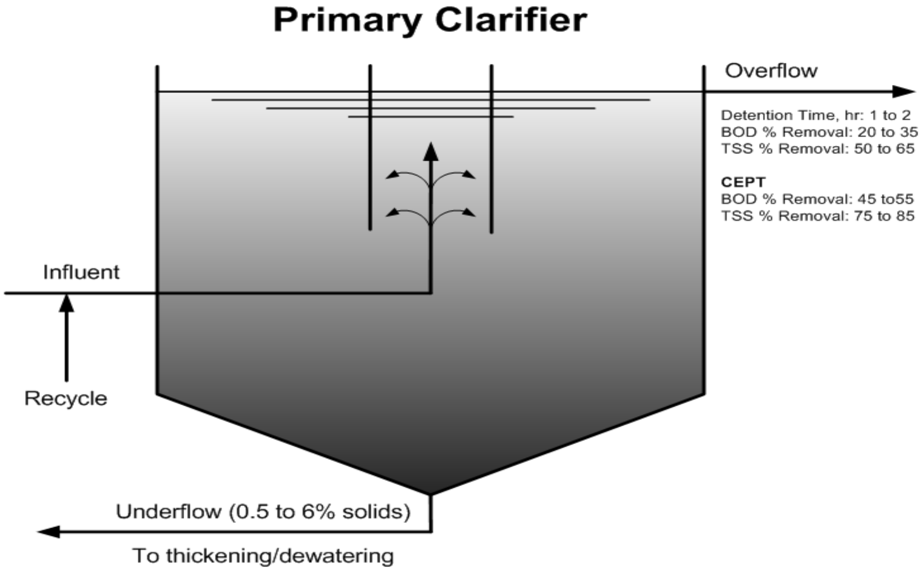


Fig (3.5) Primary clarifiers design

- Design flow rate ($Q_d = 60000 m^3/d$)
- Settling velocity (u = 26 $m^3/m^2.d$)
- Four circular clarifiers
- Depth = 3.5m +0.2 free board

Step 1 : Determine surface area A

$$A = Q_d/4/u$$

$$= 60000(m^3/d)\ /\ 4\ /\ 26(m^3/m^2 .d)$$

$$= 576.92m^2$$

Step 2 : Determine the tank radius (r)

$$\pi r^2 = 576.92m^2$$

$$r = 13.55m$$

$$d = 27.10m$$

$$A = \pi/4 * (28m)^2$$

$$= 615.75m^2$$

Step 3 : Check over flow rate (OFR)

$$OFR = Q_d \,/\, A$$

$$= \frac{1500m^3}{d} / 615.75m^2$$

$$= 24.36m/d \quad which \quad < \quad 26m/d$$

Step 4 : Determine detention time (τ)

$$\tau = A * d \,/\, Q$$

$$= 615.75(m^2) * 3.7m \,/\, 15000(m^3/d)$$

$$= 3.645hr \;>\; 1.5\ hr\ so\ it\ is\ ok$$

3.3.4 – Design calculation for the aeration tank

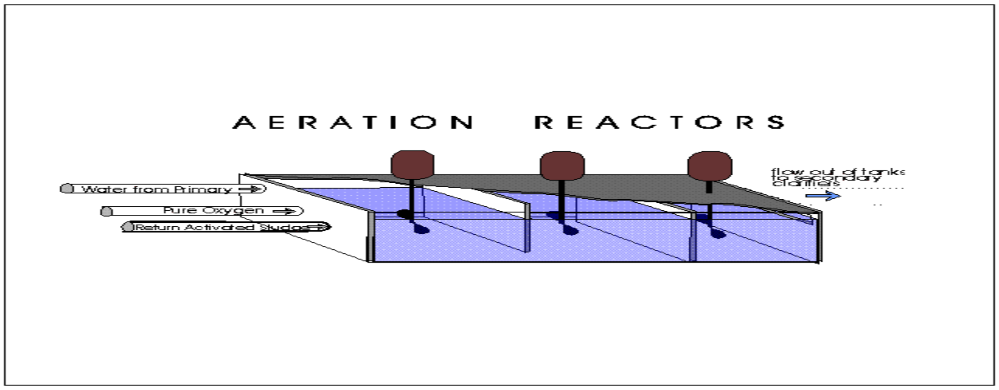


Fig (3.6) : Aeration tank design

- Design flow rate = 60000m^3/d
- Raw waste water BOD$_5$ = 200mg/l
- Raw waste water TSS = 200mg/l
- Effluent BOD$_5$ <= 20mg/l
- Effluent TSS <=20mg/l
- Waste water temperature 20c^0

BOD$_5$ and TSS removal in the primary clarifiers are 35% and 65% respectively

Step 1 : Determine BOD and TSS loading to the plant

$$BOD\ loading\ =\ 0.200Kg/m^3\ *\ 60000m^3/d\ =\ 12000Kg/d$$

$$TSS\ loading\ =\ 0.200Kg/m^3\ *\ 60000m^3/d\ =12000Kg/d$$

Step 2 : Determine BOD and TSS removed in primary sludge

$$BOD\ removed\ \ =\ 12000Kg/d\ *\ 0.35\ =\ 4200Kg/d$$

$$TSS\ removed\ =\ 12000Kg/d\ *\ 0.65\ =\ 7800Kg/d$$

Step 3 : Determine sludge flow rate

$$s.f.r\ \ =\ 7800/\ (1.05\ *1000)\ \ /\ 0.044$$

$$=\ 168.83m^3/d$$

Step 4 : Determine flow BOD and TSS in primary effluent

(Secondary influent)

$$flow\ (Q) = 60000m^3/d - 168.83m^3/d$$

$$= 59831.17m^3/d$$

$$BOD = S_O = 12000 - 4200 = 7800Kg/d$$

$$= 7800(Kg/d) * 1000 / 59831.17(m^3/d)$$

= 130.36mg/l

$$TSS = 12000 - 7800 = 4200kg/d$$

$$= 4200(Kg/d) * 1000 / 59831.17\ (m^3/d)$$

$$= \frac{70.19mg}{l}$$

Step 5 : Determine the BOD escaping treatment , S , in the effluent

$$Biodegradable\ effluent\ solid = 20mg/l * 0.63 = 12.6mg/l$$

$$Ultimate\ BODu = 12.6mg/l * 1.42mgO2/mg$$

$$= 17.892mg/l$$

$$BOD5 = 0.67 * BODu = 0.67 * 17.892 = 11.987mg/lSolve\ for\ influent\ BOD\ escaping\ treatment$$

$$20mg/l = S + 11.987mg/l$$

$$S = 8.0123mg/l$$

Step 6 : Determine treatment efficiency E

$$E = (S_O - S) / S_O * 100$$

1-The overall plant efficiency including primary treatment

$$E = (200 - 20)/200 * 100$$

$$= 90\%$$

2-The efficiency of biological treatment based on soluble BOD

$$E = (130.36 - 8.0123)/130.36 * 100$$

$$= 93.85\%$$

Step 7 : Determine the volume of the tank V

$$V = \theta_C * Q * Y * (S_O - S) / x * (1 + K_d * \theta_C)$$

Where :

$$X = value\ of\ MLVSS = (2000 mg/l)$$

Y yield coefficient for conversions of BOD5 into

bacteria = 0.6mg VSS /mg BOD_5

$$K_d = decay\ rate\ of\ bacteria\ (0.06/d)$$

$$\theta_C = cell\ residence\ time = (10 day)$$

$$V = 10 day * 59831.17\, m^3/d * 0.6 * (130.36 - 8.0123) /$$

$$2000(mg/l) (1 + 0.06/day * 10 day)$$

$$V = 13276m^3$$

Step 8 : Determine the dimension of the aeration tank

$$W / L = 0.5$$

$$d = 4.4m \ with \ 0.6 \ free \ board$$

$$V = W * L * d$$

$$13276m^3 = W * 2W * 4.4 * 4$$

$$W = 19.42m$$

$$L = 38.84m$$

$$D = 4.4 + 0.6 = 5m$$

Step 9 : Determine the sludge wasting flow rate from aeration tank $\boldsymbol{Q_W}$

$$\theta c = V * X / (Q_W * X + Q_e * X_e)$$

Where :

Q_e = flow of treated effluent (m^3/d)

X_e=microorganism concentration (VSS)influent (mg/l)

Q_W = flow of waste sludge removed from the tank (m^3/d)

$$10day\ = 13276m^3 *\ 2000(mg/l)\ /\ (\ Q_W * 2000\left(\frac{mg}{l}\right) + 59831.17(m^3/d) * 0.8 * 20(mg/l))$$

$$Q_W =\ 848.95m^3ld$$

Step 10 : Determine observed yield Y_{obs}

$$Y_{obs}\ =\ Y\ /\ (1\ + K_d * \theta_C)$$

$$=\ 0.6\ /\ (\ 1\ +\ 0.06 * 10\ \ )$$

$$= 0.375$$

Step 11 : Determine net waste activated sludge (VSS) , Kg/d

$$P_X\ =\ Y_{obs}\ *\ Q\ *\ (\ S_O - S)\ */1000(g/Kg)$$

$$= 0.375\ \ * 59831.17\frac{m^3}{d} *\ (\ 130.36 - \ 8.0123\ \ )mg/l\ /\ (1000g/Kg)$$

$$=\ 2745.211Kg/d$$

Step 12 : Determine the increase in MLSS (P_{SS})

$$P_{SS}\ =\ 2745.211(Kg/d\ )/0.8$$

$$=\ 3431.51Kg/d$$

Step 13 : Determine TSS lost in the effluent (P_e)

$$P_e\ =\ (59831.17 -\ 848.95\ )\ * 20\ /1000g/Kg$$

$$= 1179.64 Kg/d$$

Step 14 : Determine the amount of sludge that must be wasted (WAS)

$$WAS = P_{SS} - P_e$$

$$= 3431.51 - 1179.64$$

$$= 2251.86 Kg/d$$

Step 15 : Determine return activated sludge rate Q_r

$$Q_r * X_r = X * (Q_r + Q)$$

$$X_r = 0.8 * 10{,}000 mg/l = 8000 mg/l$$

$$Q_r * 8000 mg/l = 2000 mg/l * (Q_r + 59831.17)$$

$$Q_r = \frac{19943.723 m^3}{d}$$

Step 16 : Check hydraulic retention time HRT

$$HRT = V / Q$$

$$= 13276 m^3 / 59831.17 \, (m^3/d) * 24 (hr/d)$$

$$= 4.8 hr \ which \ (3 < HRT < 5)$$

Step 17 : Check F/M ratio

$$F/M = (S_O - S) / HRT / X$$

$$= \ (130.36 - 8.0123) \,/\, 0.2d - 1 \,/\, 2000mg/l$$

$$= \frac{0.293}{d} \ \ which \ \left(0.2 < \frac{F}{M} < 0.6\right)$$

Step 18 : Check organic loading rate and ultimate BOD_U

$$Loading \ = \ Q \ * \ S_O \,/\, V$$

$$59831.17\left(\frac{m^3}{d}\right) * 130.36\left(\frac{mg}{l}\right)/13276m^3 \ * 1000$$

= 0.587Kg $BOD_5/m^3.d$

$$BOD_U \ = \ Q * \ (S_O - S\,)/\ 0.67$$

$$= \ 59831.17 \ * \ (130.36 - 8.0123) \,/\, 0.67 \ * \ 1000$$

$$= 10925.69kg/d$$

Step 19 : Determine the theoretical oxygen required

Where : weight air is 1.202Kg/m^3 and contain 23.2% oxygen

$$O_{2\,req} = \ Q \ * \ ((\,S_O - S)/(1000 * f)) - 1.42 * P_X$$

Where :

f = conversion factor for converting BOD_5 TO BOD_U = 0.67

$$O_{2\,req} \ = 10925.69 \ - \ 1.42 \ * (2745.21)$$

$$= \ 7027.48Kg/d$$

Step 20 : Determine the volume of air required

$Where: weight\ air\ \ is\ 1.202kgm^3\ and\ contain\ 23.2\%\ oxygen$

$$Air\ required\ = \ 7027.48(\ Kg/d)/\ (1.202Kg/m^3 * 0.232)$$

$$= \ 25200.39m^3/d$$

$1\_the\ actual\ air\ required\ at\ 8\%\ Oxygen\ transfer\ efficiency$

$$Air\ = \ 25200.39m^3/d\ /\ 0.08$$

$$= \ 315004.925m^3/d$$

$2 -\ the\ design\ air\ required\ with\ factor\ 2$

$$Air\ = \ 218.75m^3/min\ * \ 2$$

$$= \ 437.5m^3/min$$

3.3.5- Design calculation of secondary clarifiers

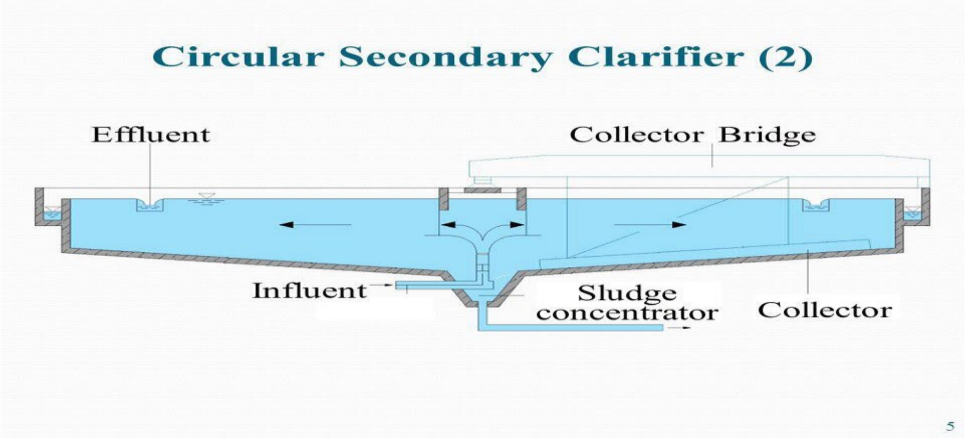


Fig (3.7) : Secondary clarifiers design

- Four circular clarifiers
- The over flow rate should be from (15 – 40)m^3 /m^2.d
- The depth = 3.5 m with 0.5 free board

Step 1 : Determine flow of secondary clarifiers Q

$$Q = Qtreated + Qr - Qw$$

$$= 59831.17 + 19943.723 - 848.95$$

$$= 78925.94 m^3/d$$

Step 2 : Determine surface area of secondary clarifiers A

$$Assume\ SOR = 15\, m^3/m^2 . d$$

$$A = Q/4 / SOR$$

$$= 78925.94(m^3/d)/4/ 15(m^3/m^2 . d)$$

$$= 1315.43\, m^2$$

$$A = \pi/4 * D^2$$

$$D = 40.92m$$

Step 3: Determine actual area

$$A = \pi/4 * 412$$

$$= 1320.254 m^2$$

Step 4 : Check the over flow rate at design flow

$$Over\ flow\ rate\ = 19731.48(m^3/d)/1320.254m^2$$

$$= 14.8m/d \quad which\ is\ < 15m/d$$

Step 5 : Determine volume of clarifiers

$$V = A * d$$

$$= 1320.254m^2 * 4m$$

$$= 5281.06\ m^3$$

Step 6 : Determine detention time θ

$$\theta = V / Q$$

$$= 5281.06m^3 / 19731.48\ m^3/d$$

$$= 0.267day = 6.423hr$$

3.3.6- Sludge calculation

S.G of sludge = 1.05g/cm^3

Solid content = 4.4%

TSS = 7800Kg/d

Step 1 : Determine Volume of sludge

$$= 7800/ (1.05 * 1000) /0.044$$

$$= 168.83m^3/d$$

Step 2 : Determine volume of sludge

Waste water sludge = 2251.86Kg/d

$$Volume = 2251.86/\ (1.05 * 1000)/0.044$$

$$= 48.74m^3/d$$

Step 3 : Determine total volume of sludge

$$VT = 48.74 + 168.83$$

$$= 217.571m^3/d$$

Step 4 : Design calculation for gravity thickener

Drying ratio = 5%

Hydraulic loading = 16m/d

$$A = 217.571(m^3/d)\ /\ 16(m/d)$$

$$= 13.59m^2$$

$$D = \left(4 * \frac{13.59m^2}{\pi}\right)^{\frac{1}{2}}$$

$$= 4.16m$$

3.4-Tertiary treatment :

3.4.1-Nitrification and de-nitrification :

Temperature = 20 °C

PH = 8

Minimum Dissolved oxygen concentration n= 2mg/l

MLSS = 2000 mg/l

NH3-N concentration (N)= 15 mg/l

Total Kjeldahl Nitrogen influent (TKN) = 30mg/l

Total Kjeldahl Nitrogen effluent (TKN) = 1mg/l

$peak\ nitrosomonas\ growth\ rate\ \mu N =\ 0.47/d$

Step 1 : Determine $\boldsymbol{MN}$: $\boldsymbol{Nitrosomonas\ growth\ rate}$ $(\frac{\mathbf{1}}{\boldsymbol{day}})$

$$KN\ =\ 10(0.051T - 1.158)$$

$$=\ 0.7277mg/l \qquad as\ N$$

$$KN : half\ saturation\ constant\ \left(\frac{mg}{l}\right) as\ NH3 - N$$

$$TCF = e^{(0.098T-15)}$$

$$Temperature\ correction\ factor\ =\ \ 1.63$$

KO_2 : half saturation constant oxygen (1.3mg/l)

$$MN\ = \mu N * 1.63 * \left(\frac{N}{KN + N}\right) * \left(\frac{D0}{KO2 + D0}\right) *$$
$$(1 - 0.833(6.2 - PH))$$

$$=\ 0.47\ * 1.63 * \left(\frac{1}{0.727 + 1}\right) * \left(\frac{2}{1.3 + 2}\right) * (1)$$

$$=\ 0.268/d$$

Step 2 : Determine ammonia oxidation rate mg NH3-N oxidized /mg VSS . d $(\boldsymbol{RN})$

YN : Organism yield coefficient mg nitrosamines grower VSS/ mg NH_3-N removed

$$YN\ =\ 0.2\ \ from\ table\ (6.23)$$

$RN = MN / YN$

$= 0.268 / 0.2$

$= 1.344 /d$

Step 3 : Determine minimum cell residence time θc

$1/\theta c = Y * Kl - Kd$

$Y = YN = 0.2$ from table (6.23)

$Kl = RN = 1.45 /d$ from step 2

$1/\theta c = 0.2 * 1.344 - 0.05$

$= 0.2188/d$

$\theta c -$ min $= 1/0.2188$

= 4.57day

Step 4 : Determine solid retention time from another rough θc

$\Theta d = 1 / MN$

$= 1 / 0.268$

$= 3.72 day$

Step 5 : Determine design cell residence time

$\Theta c - d = safety\ factor * \theta c$

$= 2.5 * 4.57$

$= 11.425\ day$

Step 6 : Determine utilization U

$U = 1/Y * (1/\theta C - d + Kd)$

$= 1/0.2 * (1/11.425 + 0.05)$

$= 0.687 /d$

Step 7 : Determine organic BOD removal rate U

$From\ table\ (6.12)\ in\ appendix\ (B.6)$

$Y = 0.6 kg\ Vess/\ kg\ BOD$

$K = 0.06\ /d$

$1/\theta c - d = y * U - k$

$1/11.425 = 0.6 * U - 0.06$

$U = 0.2458\ kg\ BOD\ removed\ /\ kg\ MLSS$

$Assume\ E = 90\ \%\ removed$

$$\frac{F}{M} = \frac{0.2458}{0.90} = 0.2731\ kg\ BOD\ \frac{removed}{kgMLSS.d}$$

Step 8: Determine hydraulic time for organic and ammonia oxidation

$Assume\ 80\%\ of\ MLSS\ is\ nitrification$

$\Theta = (S0 - S)/UX$

$= (130.36 - 8.0123) / 0.2458 * 0.8 * 2000$

$= 0.311\ d$

$= 7.464 hr\ for\ organic$

Step 9 : Determine the steady ammonia concentration at

The effluent

$U = RN * N / (KN + N)$

$0.687 = 1.344 * N / (0.727 + N)$

$N = 0.76\ d = 9.83 hr$

$\Theta = (N0 - N) / U\ X$

$$= (30 - 0.76) / 0.687 * 2000 * 0.8$$

$$= 0.0266\, d$$

Step 10: Determine the volume V of aeration tank required based on organic removal process

$$V = Q * \theta$$

$$V = 2500 m^3/hr * 7.464 hr$$

$$= 18660\, m^3$$

Step 11 : Determine BOD loading rate

$$Q = 60000 m^3/d * 130.36 mg/l/1000$$

$$= 7821.6 kg/d$$

$$BOD\ rate = 7821.6 (kg/d)/18660 m^3$$

$$= 0.419 \quad which\ is\ below\ the\ range\ (0.8\ to\ 1.92)$$

Step 12 : Determine sludge waste

$$\Theta c = VX / (QW\, X + Qe\, Xe)$$

$$Xe = 20 * 0.8 = 16\, mg/l$$

$$Qe\, Xe = 16 mg/l * 60000 m^3/d /1000$$

= 960kg/d

$$V\, X / \theta C = 18660 m^3 * 0.8 * 2000 / 11.425 d/1000$$

$$= 2613.216 kg/d$$

$$QW\, X = 2613.216 - 960 = 1653.216 kg/d$$

3.4.2-Design chlorine tank (disinfection)

3.4.1

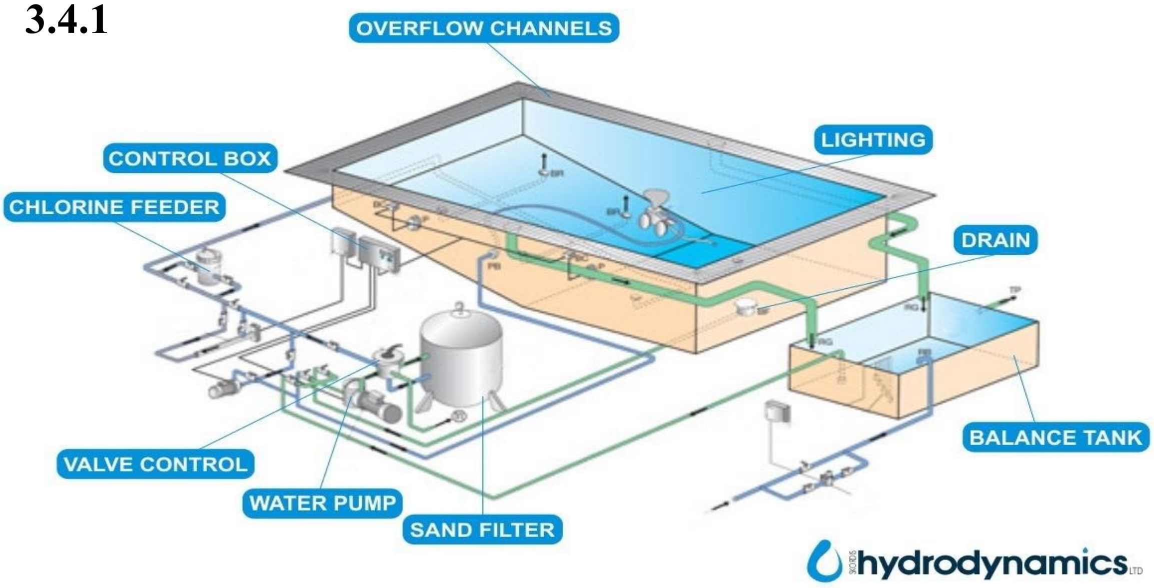


Fig (3.8) : Chlorine tank design

Step 1 : In 20min kill 99.9% of bacteria when treated 5 mg/l of chlorine

$Nt/N0 = (1 - 0.999) /100 = 0.001$

Chick's Law (1908)- most widely used :

$dN/dt = -k * N$

$Ln (0.001) = -k * t$

Where :

t = time between (20_30) min

k = First order susceptibility coefficient

Nt = concentration of living microorganism at time t

$N0$ = concentration of living microorganism at time 0

$Ln(0.001) = -K * 20min$

$K = 0.345/min$

Step 2 : Assume plug flow

$In - out + generation = accumalation$

Assume steady state

$Q\ dN + (-rN)\ dV = 0$

Where:

$-r = K * N * \theta$

$\Theta = V/Q$

$d\theta = dV/Q$

$QdN + (K * V * \theta) * (d\theta * Q) = 0$

$dN + (K * V * \theta)d\theta = 0$

$dN = -K * N * \theta * d\theta$

$dN/N = -K * \theta * d\theta$

$Ln(N/N0) = -K * \theta 2/2$

Step 3 : Determine volume of chlorine tank V

$Ln(0.001) = -0.345 * \theta 2/2$

$$\Theta = 6.32min$$

$$V = Q * \theta$$

$$= 0.694m^3/s * 6.32min * 60s/min$$

$$= 263.1648m^3$$

Chapter four (4)

Analytical methods used in Petroleum Refinery wastewater analysis

4.1 Methodology:-

The methodology followed in this research amounts to

- Field visits and observation.
- Discussion with refinery personal concerned with wastewater treatment unit.
- Experiment lab work wastewater analysis.

4.2The experiment lab work includes:

1- Oil Content.
2- Phenol Content.
3- Ammonia Nitrogen.
4- Sulfide.
5-Sludge volume (S.V).
6- Sludge volume Index (S.V.I).
7-Dissolved Oxygen (DO).
8-Ortho-phosphate Content.
9-Suspended Solid.
10-Biochemical Oxygen Demand (BOD).
11-Chemical Oxygen Demand (COD).

4.2.1 Oil content:

Instrument:

- Ultraviolet spectrophotometer.

- Separating funnel = 500ml.

- Funnel diameter is 60mm.

- Measuring flash.

Figure (4.1): Ultraviolet spectrophotometer

Calculate the analysis result.

Calculate the oil content:

A= oil content correspondingly to relative absorbency.

V= volume of water sample ml.

$$A = Reading * 7.03\ 0.02 * 200 / v$$

4.2.2 Hydroxyl Benzene (phenol) content:

Instruments:

- 500ml whole glass vaporizer.
- Spectrophotometer.

Figure (4.2): Ultraviolet spectrophotometer

Result expression:

$$Phenol\ content\ (mg/l = absorbance\ (Reading\ )\ * 196.15 *\ 0.11/v$$

V= sample volume in ml.

4.2.3 Ammonia Nitrogen:

Instrument: - Vaporize composed of distillation flask of 500-800ml blow out prevention nozzle and vertical condensation tube, the end o condensation tube can be connected with a burette with proper length, dip the outlet tip below 2cm of absorption liquid level.

Result:

$$CN\ = V1 - V2\ /V0 *\ C * 14.01 * 1000$$

Where:

V_0 = sample volume in ml.

V_1 = volume of standard hydrochloric acid solution consumed for titrating sample in ml.

V_2 = volume of standard hydrochloric acid solution for titrating blank

Sample in ml.

C = concentration of standard hydrochloric acid titration solution

4.2.4 Sulfide (Iodimetric Method):

Instruments:

- Acid burette.
- Iodine flask.
- Vacuum pump, Buckner filter.
- Middle-speed quantitative filter paper.

Result:

$$S^{-2}\ (ml/l) = (V1 - V2) * C * 16 * 1000 / v$$

Where:

V_1 = volume of Sodium hyposulfite standard solution for blank test (ml).

V_2 = volume of Sodium hyposulfite for titrating water sample (ml).

V = volume of water sample (ml).

4.2.5 Sludge Volume (S.V):

Definition:

The volume, which is occupied by 100ml sludge mixture through half hour sediment, is called sludge volume.

Instrument:

- Measuring cylinder = 1000 ml.

Calculation:

The formula is as the following:

$$Sludge\ volume\ \% = sludge\ volume\ after\ sediment\ (ml) * 100\ /Volume\ of\ mixture\ liquid$$

4.2.6 Sludge Volume Index (S.V.I):

Result:

$SVI\ = S\,.V/(W1 - W2)$

4.2.7 Dissolved Oxygen (DO) Iodimetric Analysis:

Instruments:

- A narrow mouth glass bottle with volume of 250ml-300ml.

Result:

For (C): $C1\ =\ 2.8 * V$ For (F): $C2\ =\ 3.08 * V$

$C1 \equiv\ content\ of\ soluble\ Oxygen\ (mg/l)$.

4.2.8 Determination of Ortho-phosphate Content:

Ammonium molybdate spectrophotometer

Instruments:

- Spectrometer with 1cm thick absorption cell.

Results:

$X\ (mg/l)\ =\ 260\ * Reading\ *\ 0.34\ /V$

V = volume of transferred test solution, expressed in ml.

4.2.9 Determination of Suspended Solid (Weighting Method):

Instruments:

- Analysis balance: reciprocal sensibility of 0.001mg.
- Drying box with constant temperature.

- Dryer.
- Glass funnel.
- Measuring bottle: high type.
- Low-speed filter paper.

Calculations of analysis result:

$$X = (W2 - W1) * 1000 * 1000 / Vw$$

Where;

X= suspended matter of water sample (mg/l).

W_1= weight of weighting bottle and filter paper in (g).

W_2 = weight of weighting bottle, filter paper and suspended matter in (g).

V_W= volume of water sample in (ml).

4.2.10 Biochemical Oxygen Demand (BOD):

Several methods to measure BOD values; e.g: Titration methods, by BOD track instrument, and digital re-spirometer.

Instruments:

- -Re-spirometer and incubator.
- -Amber bottles with seal caps.
- -Stopcock grease.
- -Magnetic stirrers.

4.2.11 Chemical Oxygen Demand (COD)(Titration Method):

Instruments:

- -Reflux apparatus.
- -Round bottom flask.
- -500-ml Erlenmeyer

- Volumetric cylinder.
- Glass beads.

Calculation: $COD\ mg/l = (A - B) * C * 800/sample\ volume\ ml$

Where:

A= Ferrous ammonium sulfate solution used for blank, ml

B=Ferrous ammonium sulfate solution used for sample, ml

C=Normality of ferrous ammonium sulfate solution.

Chapter (5)

Discussions, conclusions and recommendations

5.1) Discussions

1)We must separate and treat each type of water from the other types like oily water, sewage water, process water, rain water in wastewater treatment unit in zawiya petroleum refinery

2) Design activated sludge was take a big area of ground if we applied in zawiya petroleum refinery so I prefer membrane bioreactor technology

3) Zawiya petroleum refinery is very small refinery so this calculation was not suitable for wastewater treatment unit in zawiya petroleum refinery

4) All design in wastewater treatment unit is satisfactory because is between the range compared very well for world books in design wastewater treatment and the effluent within the limits allowed for environmental effluent standards of wastewater generated from a petroleum refinery

5) The most important parameter like hydraulic retention time (HRT) , it was 4.8 hr which is best time for retention bacteria and food per mass ratio (F/M) it was 0.293 which is small quantities all this indicator is means the design wastewater treatment unit is acceptable

5-2 Conclusions

The conclusion of this project can be summarized and listed as follows:

1) The design calculation was performed successfully for the selected units of a wastewater treatment plant that can treat effluent wastewater from a crude oil Petroleum Refinery (PR).
2) Design results (dimensions, volume, and quantities) of the various units in the wastewater treatment plant targeted for design calculations compared very well with those installed at the Zawiya Petroleum Refinery (ZPR).
3) The application of theoretical model equations and the analysis of the effluent wastewater generated at any Petroleum Refinery (PR) will be a good tool for preliminary design calculation for each piece of equipment in the wastewater treatment plant.

5-2 Recommendations

Through this project, the following recommendation points are extracted and need to be considered in future studies:

1) A deep Environmental Impact Assessment (EIA) need to be conducted on the effluent wastewater generated from various operations at the Zawiya Petroleum refinery (ZPR).
2) Future studies are also needed to identify the sources, type and concentrations of various pollutants generated from various operations at the Zawiya Petroleum refinery (ZPR).
3) Through this study, the treated wastewater constituents at the existing wastewater treatment plant at Zawiya Petroleum Refinery (ZPR) were not provided to be evaluated and compared to the effluent standards. It is strongly recommended for future studies to have such data available.
4) For future studies, the sludge treatment technologies and sludge disposal technologies that are very effective technically and economically need to be considered for serious investigation because of its impact on the environment around the Petroleum Refinery area. In particular, the sludge generated from the storage tanks clean up or any other operations at the Petroleum Refinery (PR) is targeted for these investigations.

5) Economic evaluations and cost estimate investigations in future are strongly recommended for Petroleum Refinery Waste water treatment plants.

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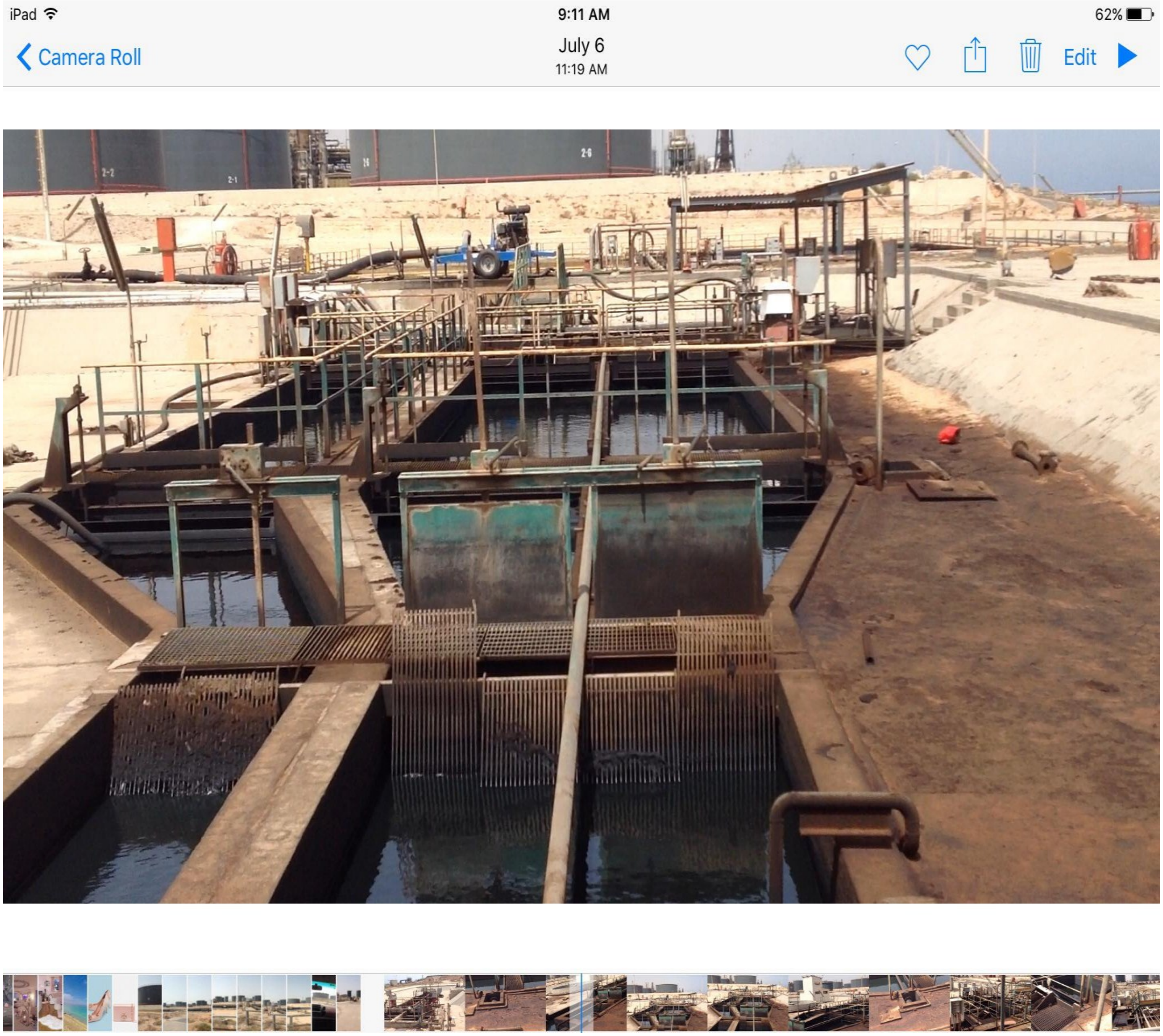
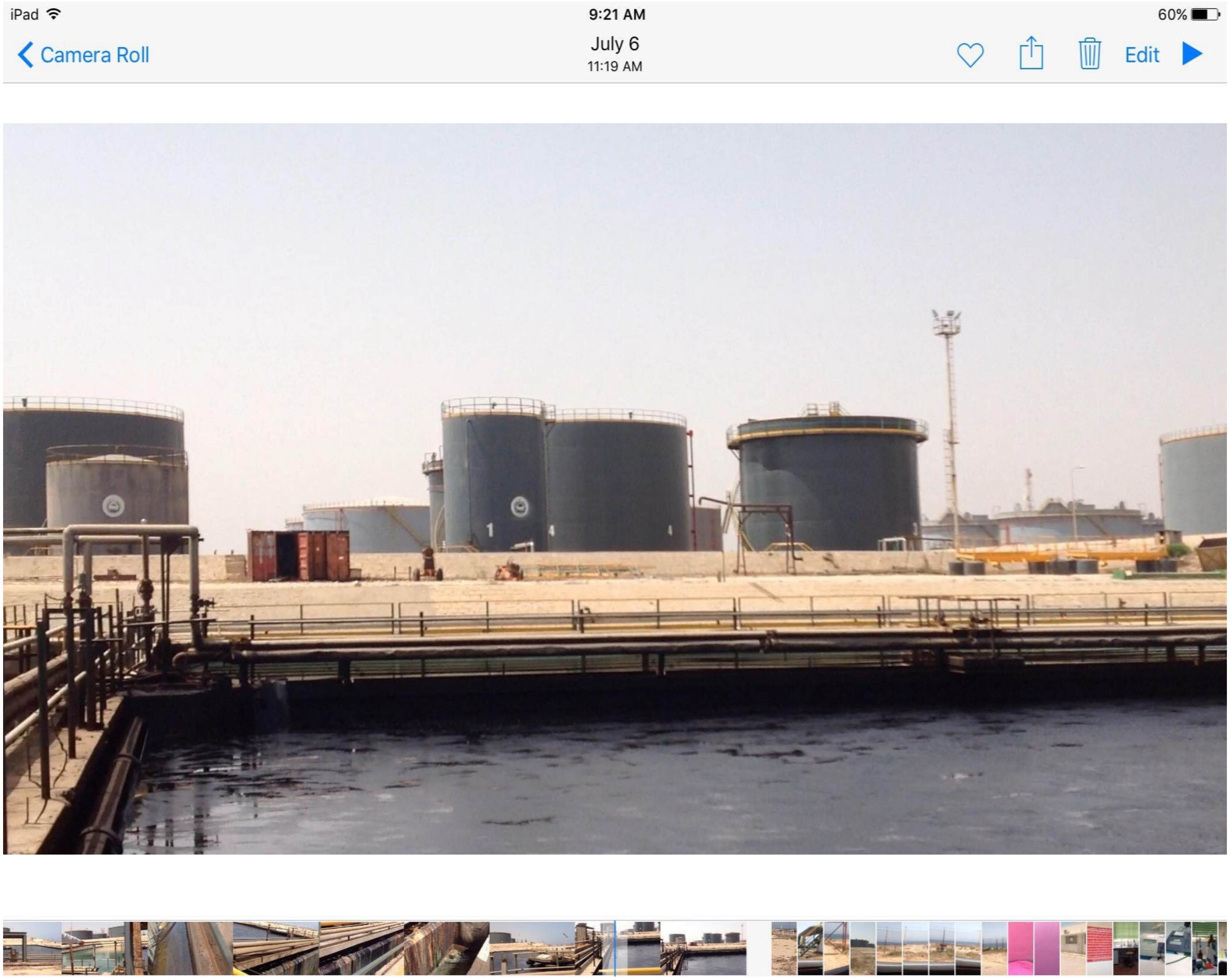
APPENDIX (A.1)

ZRC API separator

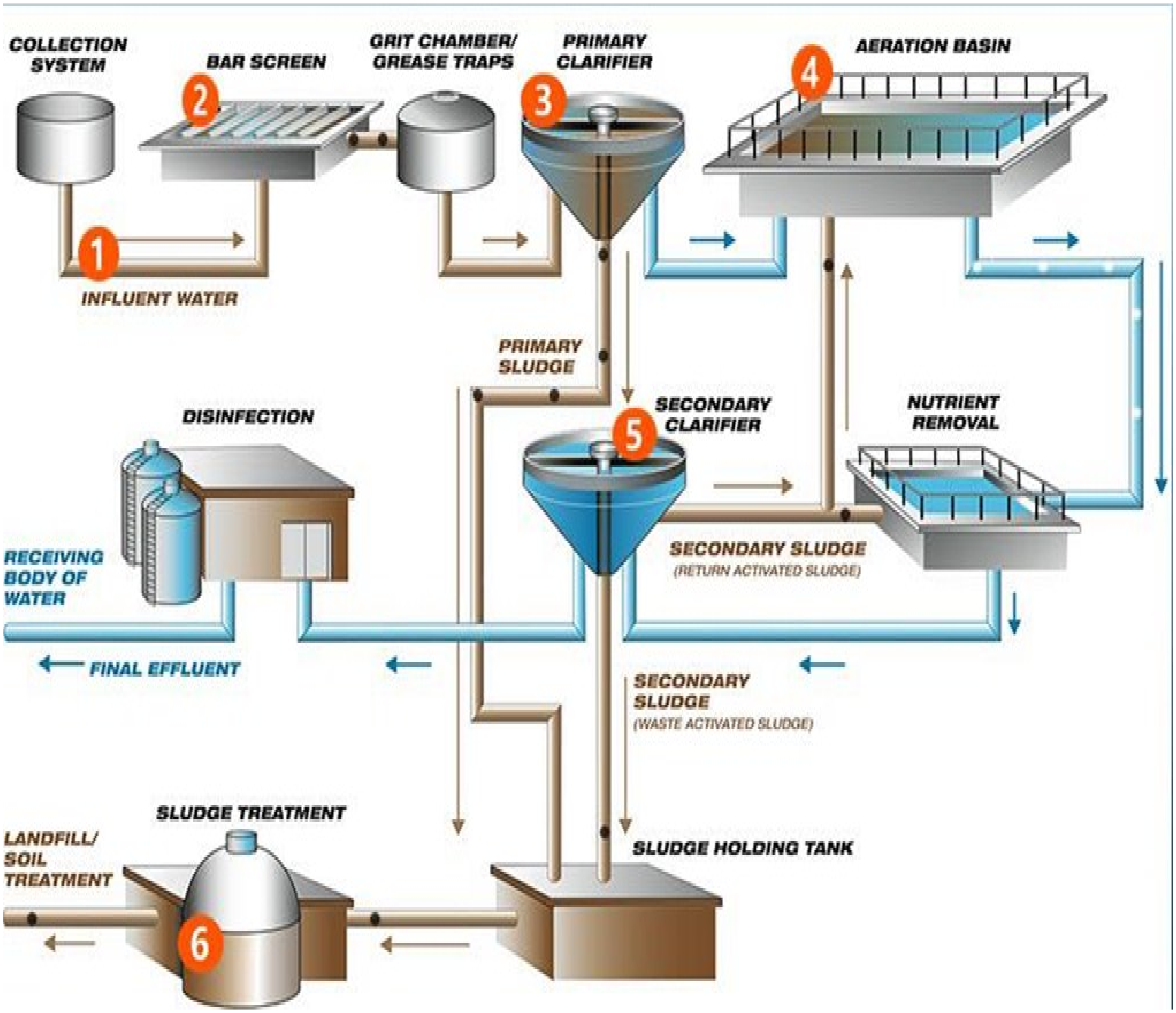


APPENDIX (A.2): ZRC Waste oil tank



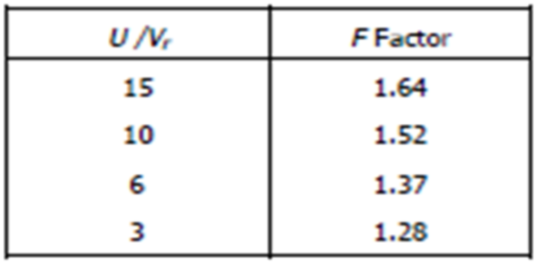
APPENDIX (A.3)

Secondary treatment (biological treatment)



APPENDIX (B.1)

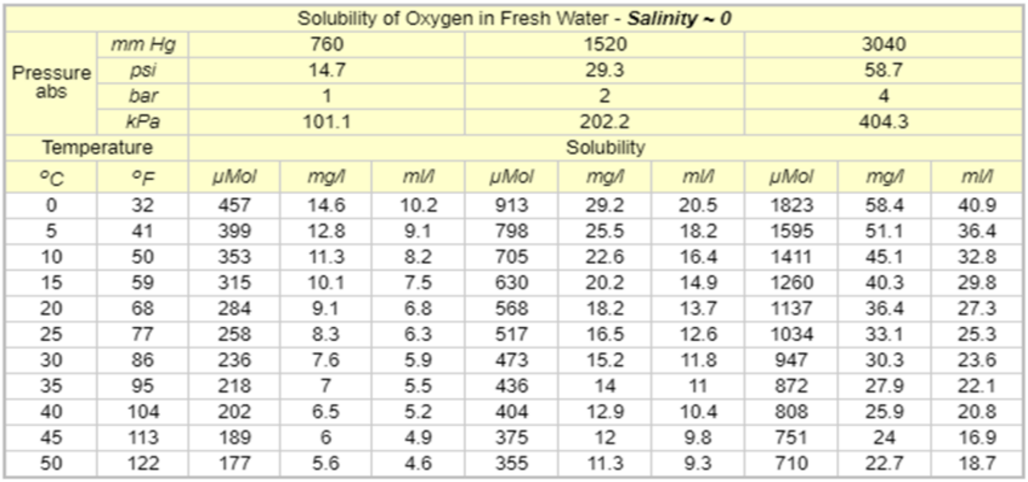
Table of F Factor for API Separators



U/V_r	*F* Factor
15	1.64
10	1.52
6	1.37
3	1.28

APPENDIX (B.2)

Table of Solubility of air in water



Solubility of Oxygen in Fresh Water - ***Salinity ~ 0***										
Pressure abs	*mm Hg*	760			1520			3040		
	psi	14.7			29.3			58.7		
	bar	1			2			4		
	kPa	101.1			202.2			404.3		
Temperature		Solubility								
°C	*°F*	*μMol*	*mg/l*	*ml/l*	*μMol*	*mg/l*	*ml/l*	*μMol*	*mg/l*	*ml/l*
0	32	457	14.6	10.2	913	29.2	20.5	1823	58.4	40.9
5	41	399	12.8	9.1	798	25.5	18.2	1595	51.1	36.4
10	50	353	11.3	8.2	705	22.6	16.4	1411	45.1	32.8
15	59	315	10.1	7.5	630	20.2	14.9	1260	40.3	29.8
20	68	284	9.1	6.8	568	18.2	13.7	1137	36.4	27.3
25	77	258	8.3	6.3	517	16.5	12.6	1034	33.1	25.3
30	86	236	7.6	5.9	473	15.2	11.8	947	30.3	23.6
35	95	218	7	5.5	436	14	11	872	27.9	22.1
40	104	202	6.5	5.2	404	12.9	10.4	808	25.9	20.8
45	113	189	6	4.9	375	12	9.8	751	24	16.9
50	122	177	5.6	4.6	355	11.3	9.3	710	22.7	18.7

APPENDIX (B.3)

table of typical design parameters for primary clarifier

TABLE 6.10 Typical Design Parameters for Primary Clarifiers

		Surface settling rate, $m^3/(m^2 \cdot d)$ $(gal/(d \cdot ft^2))$		
Type of treatment	Source	Average	Peak	Depth, m (ft)
Primary settling followed by secondary treatment	US EPA, 1975a	33–19 (800–1200)	81–122 (2000–3000)	3–3.7 (10–12)
	GLUMEB–Ten States Standards and Illinois EPA, 1998	600	Figure 6.11	minimum 2.1 (7)
Primary settling with waste activated sludge return	US EPA, 1975a	24–33 (600–800)	49–61 (1200–1500)	3.7–4.6 (12–15)
	Ten States Standards, GLUMRB, 1996	≤ 41 (≤ 1000)	≤ 61 (≤ 1500)	3.0 (10) minimum

APPENDIX (B.4)

Figure of percentage of removal in primary

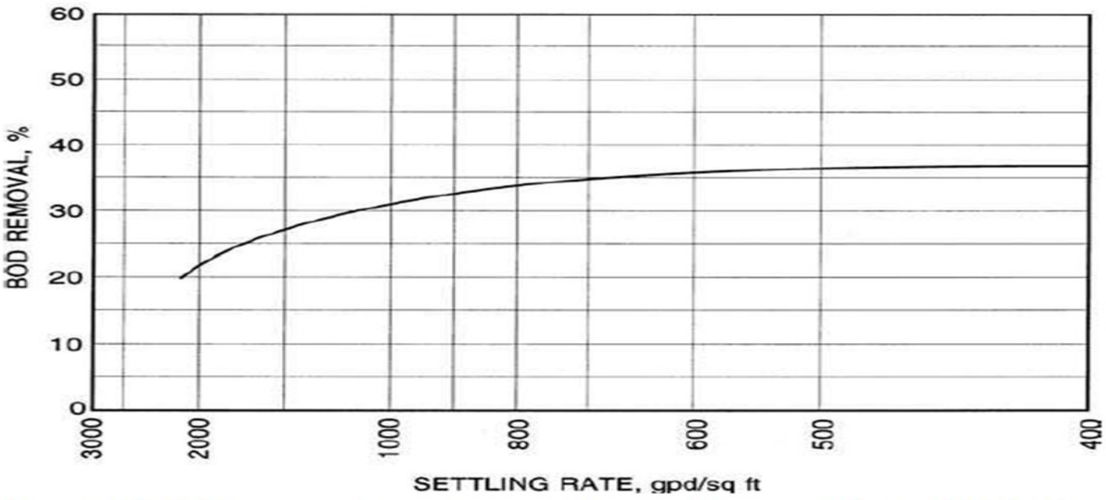


Figure 6.11 BOD_5, removal in primary settling tank *(source: Illinois EPA 1998).*

APPENDIX (B.5)

Table of Permissible aeration tank

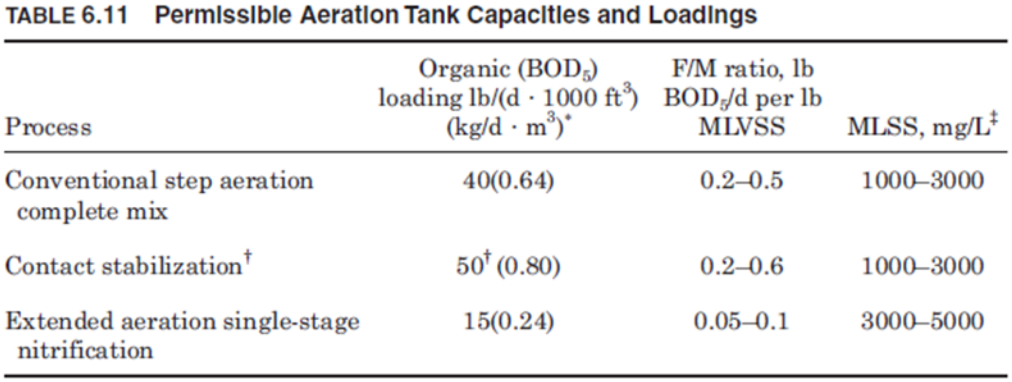


TABLE 6.11 Permissible Aeration Tank Capacities and Loadings

Process	Organic (BOD_5) loading lb/(d · 1000 ft^3) (kg/d · m^3)[*]	F/M ratio, lb BOD_5/d per lb MLVSS	MLSS, mg/L[‡]
Conventional step aeration complete mix	40(0.64)	0.2–0.5	1000–3000
Contact stabilization[†]	50[†] (0.80)	0.2–0.6	1000–3000
Extended aeration single-stage nitrification	15(0.24)	0.05–0.1	3000–5000

APPENDIX (B.6)

Table of typical parameter for biological treatment

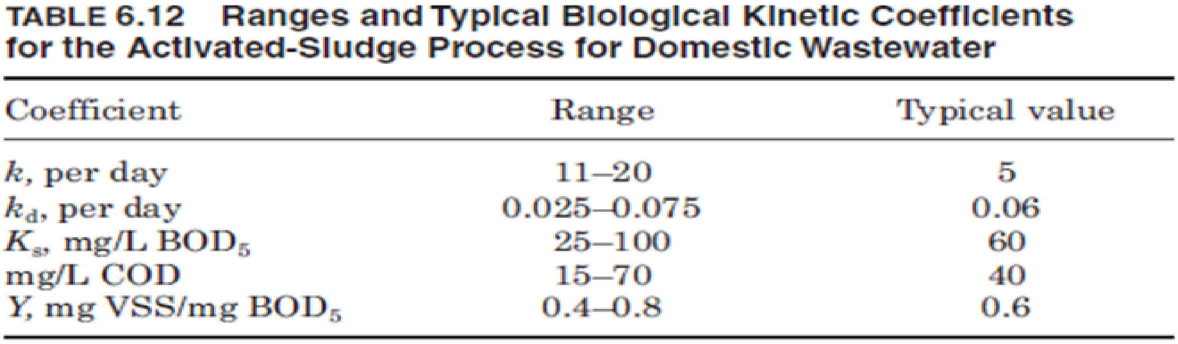
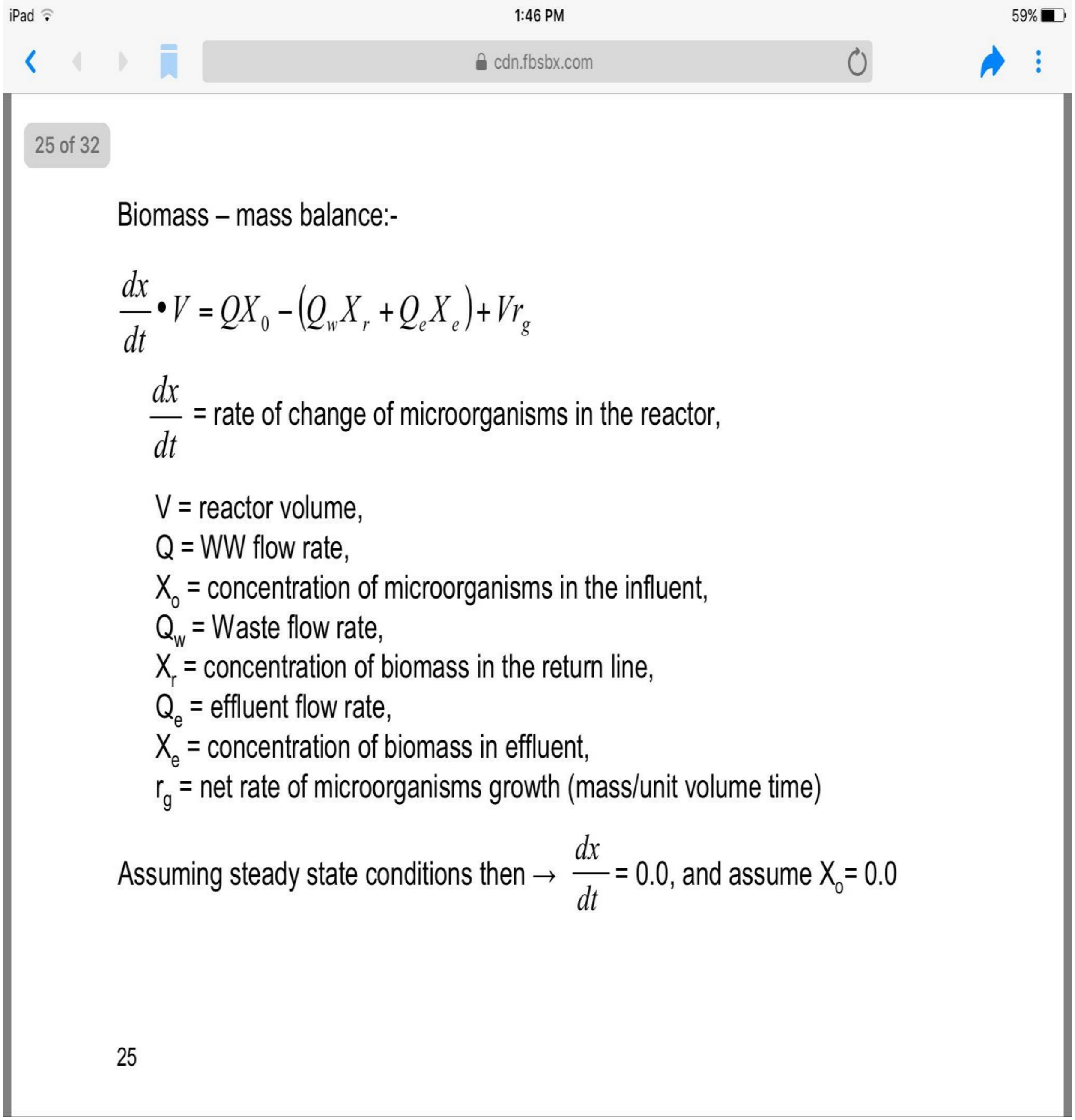


TABLE 6.12 Ranges and Typical Biological Kinetic Coefficients for the Activated-Sludge Process for Domestic Wastewater

Coefficient	Range	Typical value
k, per day	11–20	5
k_d, per day	0.025–0.075	0.06
K_s, mg/L BOD_5	25–100	60
mg/L COD	15–70	40
Y, mg VSS/mg BOD_5	0.4–0.8	0.6

APPENDIX (B.7)

Design equations related to Activated Sludge (AS) Wastewater treatment



Biomass – mass balance:-

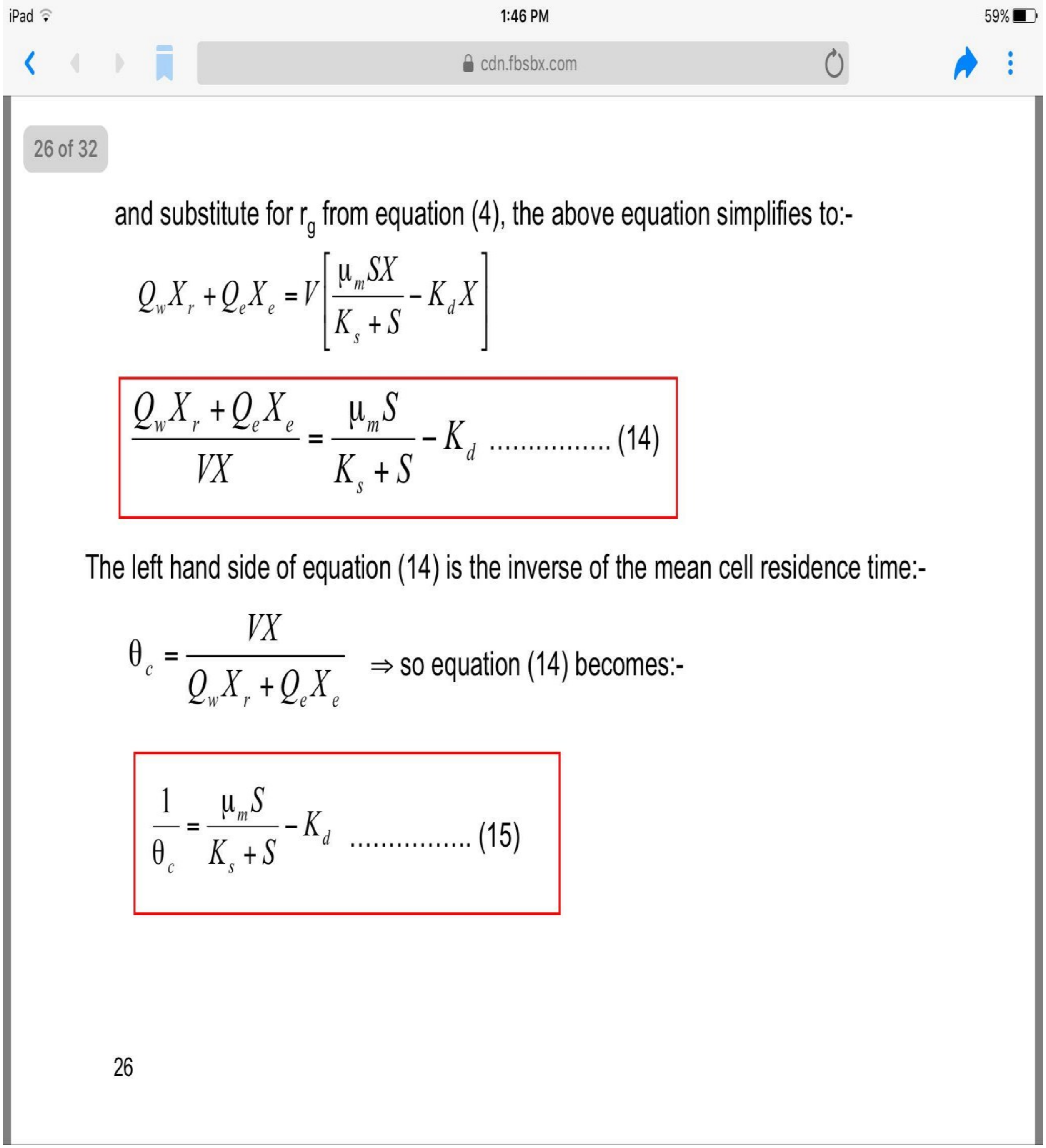
$$\frac{dx}{dt}\bullet V = QX_0 - \left(Q_wX_r + Q_eX_e\right) + Vr_g$$

$\frac{dx}{dt}$ = rate of change of microorganisms in the reactor,

V = reactor volume,
Q = WW flow rate,
X_o = concentration of microorganisms in the influent,
Q_w = Waste flow rate,
X_r = concentration of biomass in the return line,
Q_e = effluent flow rate,
X_e = concentration of biomass in effluent,
r_g = net rate of microorganisms growth (mass/unit volume time)

Assuming steady state conditions then → $\frac{dx}{dt}$ = 0.0, and assume X_o= 0.0

Appendix (B-7) (continue)



and substitute for r_g from equation (4), the above equation simplifies to:-

$$Q_w X_r + Q_e X_e = V\left[\frac{\mu_m S X}{K_s + S} - K_d X\right]$$

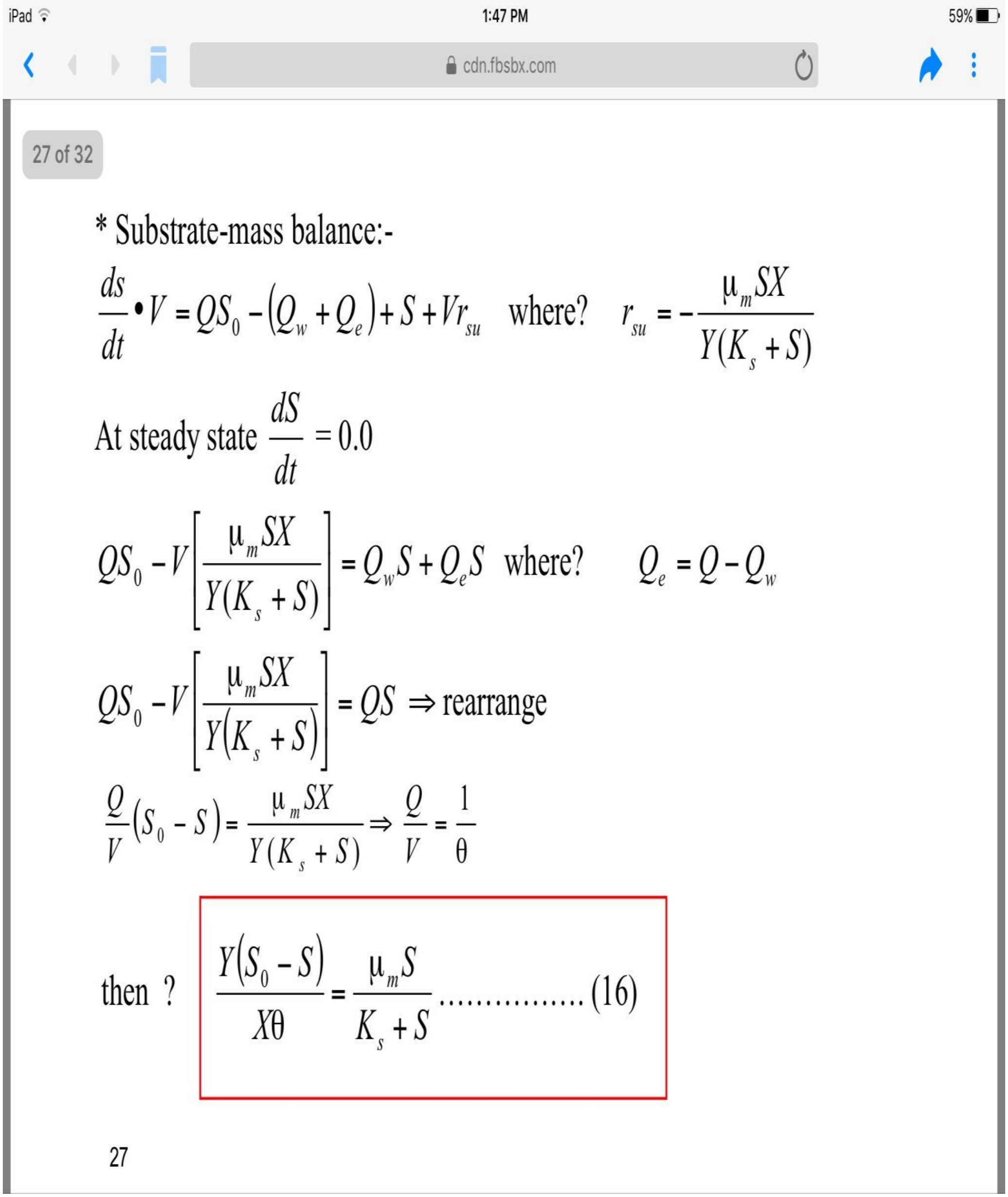
$$\boxed{\frac{Q_w X_r + Q_e X_e}{VX} = \frac{\mu_m S}{K_s + S} - K_d \quad \ldots\ldots\ldots\ldots\ldots (14)}$$

The left hand side of equation (14) is the inverse of the mean cell residence time:-

$$\theta_c = \frac{VX}{Q_w X_r + Q_e X_e} \quad \Rightarrow \text{so equation (14) becomes:-}$$

$$\boxed{\frac{1}{\theta_c} = \frac{\mu_m S}{K_s + S} - K_d \quad \ldots\ldots\ldots\ldots\ldots (15)}$$

Appendix (B-7) (continue)



* Substrate-mass balance:-

$$\frac{ds}{dt}\bullet V = QS_0 - \left(Q_w + Q_e\right) + S + Vr_{su} \quad \text{where?} \quad r_{su} = -\frac{\mu_m SX}{Y(K_s + S)}$$

At steady state $\frac{dS}{dt} = 0.0$

$$QS_0 - V\left[\frac{\mu_m SX}{Y(K_s + S)}\right] = Q_w S + Q_e S \quad \text{where?} \qquad Q_e = Q - Q_w$$

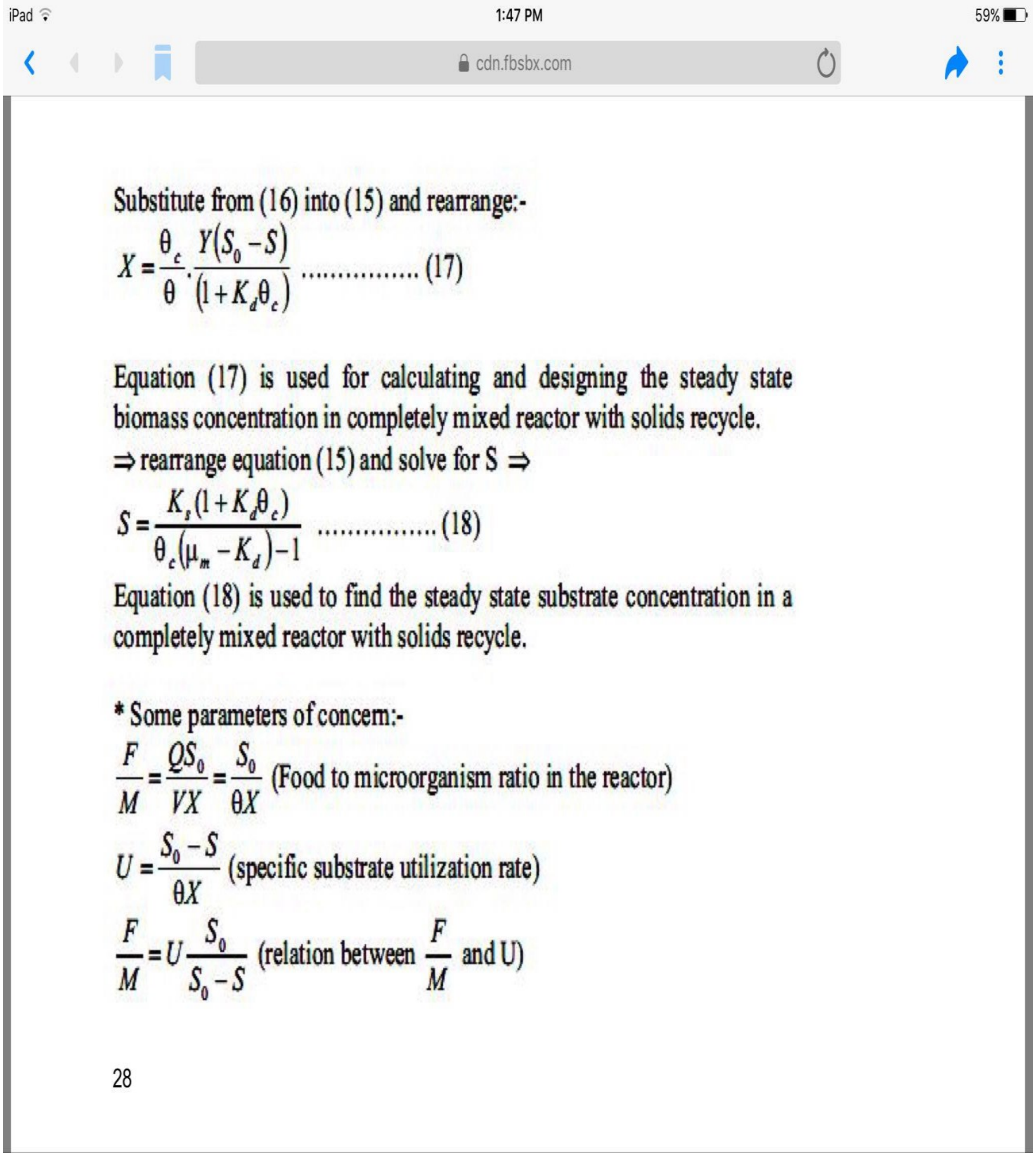
$$QS_0 - V\left[\frac{\mu_m SX}{Y\left(K_s + S\right)}\right] = QS \Rightarrow \text{rearrange}$$

$$\frac{Q}{V}\left(S_0 - S\right) = \frac{\mu_m SX}{Y\left(K_s + S\right)} \Rightarrow \frac{Q}{V} = \frac{1}{\theta}$$

then ? $$\boxed{\frac{Y\left(S_0 - S\right)}{X\theta} = \frac{\mu_m S}{K_s + S} \ldots\ldots\ldots\ldots\ldots\ldots (16)}$$

27

Appendix (B-7) (continue)



Substitute from (16) into (15) and rearrange:-

$$X = \frac{\theta_c}{\theta} \cdot \frac{Y(S_0 - S)}{(1 + K_d\theta_c)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (17)$$

Equation (17) is used for calculating and designing the steady state biomass concentration in completely mixed reactor with solids recycle.

⇒ rearrange equation (15) and solve for S ⇒

$$S = \frac{K_s(1 + K_d\theta_c)}{\theta_c(\mu_m - K_d) - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (18)$$

Equation (18) is used to find the steady state substrate concentration in a completely mixed reactor with solids recycle.

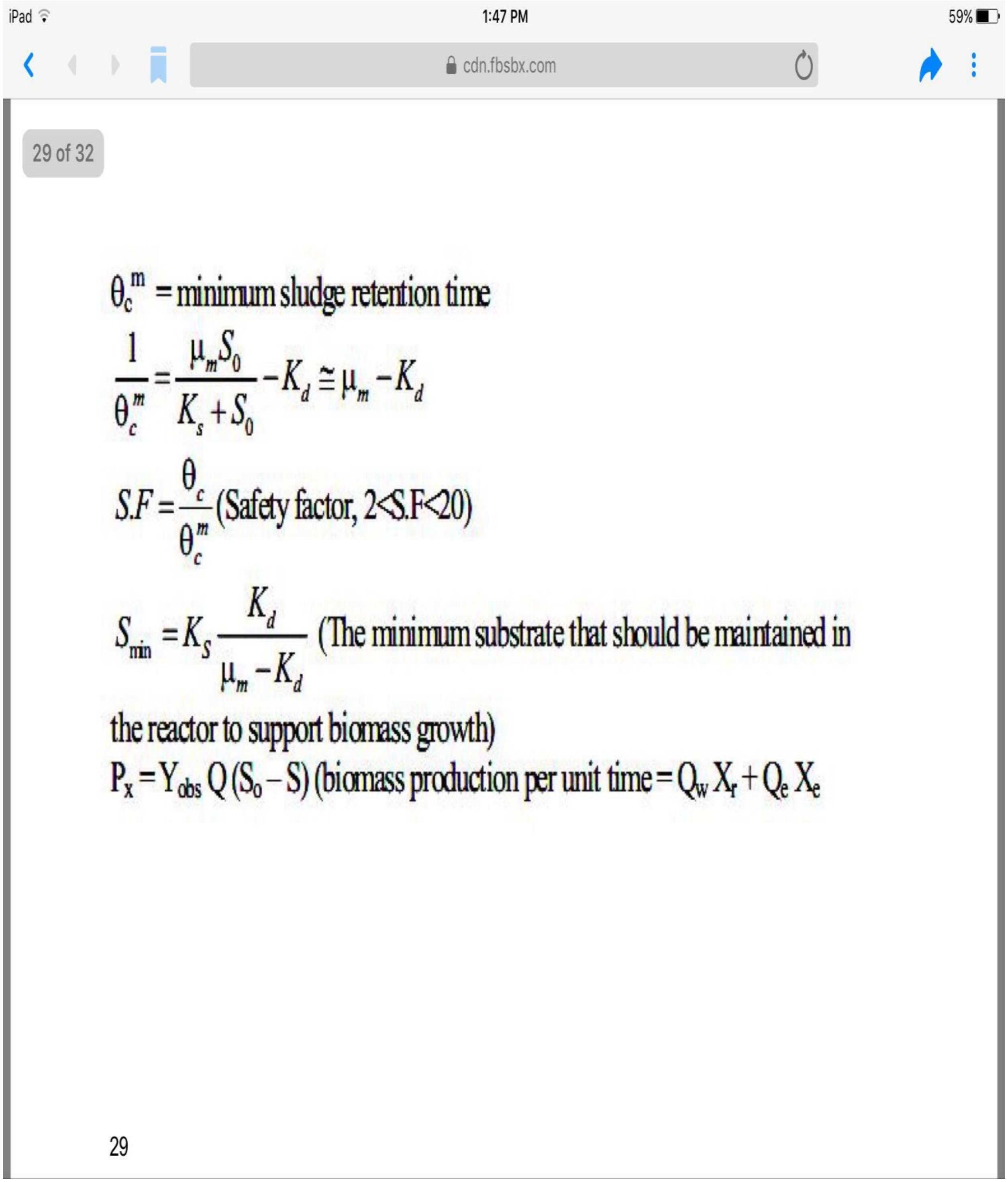
* Some parameters of concern:-

$\frac{F}{M} = \frac{QS_0}{VX} = \frac{S_0}{\theta X}$ (Food to microorganism ratio in the reactor)

$U = \frac{S_0 - S}{\theta X}$ (specific substrate utilization rate)

$\frac{F}{M} = U \frac{S_0}{S_0 - S}$ (relation between $\frac{F}{M}$ and U)

Appendix (B-7) (continue)



θ_c^m = minimum sludge retention time

$$\frac{1}{\theta_c^m} = \frac{\mu_m S_0}{K_s + S_0} - K_d \cong \mu_m - K_d$$

$$S.F = \frac{\theta_c}{\theta_c^m} \text{ (Safety factor, } 2 < S.F < 20)$$

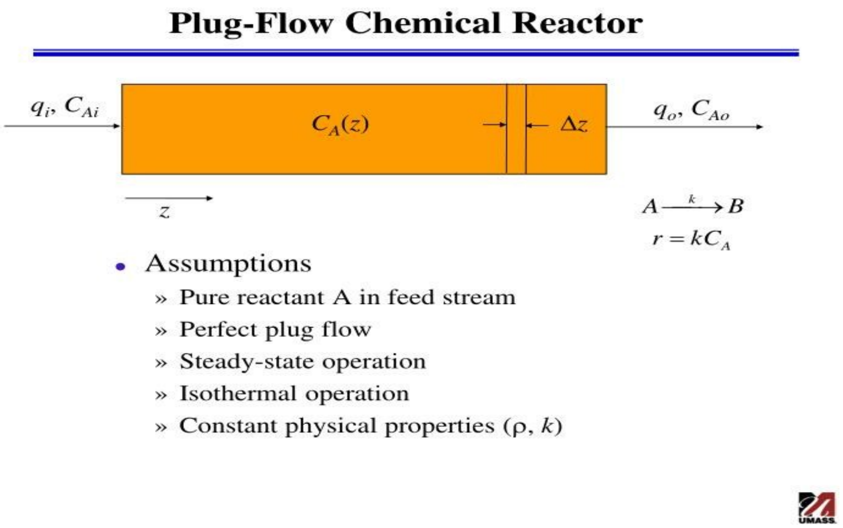
$$S_{min} = K_S \frac{K_d}{\mu_m - K_d}$$ (The minimum substrate that should be maintained in the reactor to support biomass growth)

$P_x = Y_{obs}\, Q\, (S_o - S)$ (biomass production per unit time $= Q_w X_r + Q_e X_e$

APPENDIX (B.9)

Disinfection Plug Flow Reactor (PFR) design equations

Plug flow reactor (PFR)



Plug-Flow Chemical Reactor

- Assumptions
  - » Pure reactant A in feed stream
  - » Perfect plug flow
  - » Steady-state operation
  - » Isothermal operation
  - » Constant physical properties (ρ, k)

- The materials balance around the volume element dV

$$Q*C_A = Q * (C_A - dC_A) + r_A*Dv$$

$$Q*dC_A= r_A*dV$$

- Consider a plug flow reactor with first order reaction

$$r_A = - K * C_A$$

$$\theta = V/Q$$

$$D\theta = DV /Q$$

$$\text{Then : } \int dC_A = -K \int d\theta$$

$$\theta = t$$

- Which can be integrated for a first order kinetic as follows

$$Ln(C_A/C_{A0}) = -K *(t_2 - t_1)$$

APPENDIX (C.1)

GB Standard for refinery effluents

Item	**Specification GB8978_ 88 _ Class1 New Rev.**	**Specification GB8978_ 1996 _ Class 1_ Latest Chinese Standard**	**Specification Latest EU Standard**	**Specification UK Waste Water Discharge Standard 1984**
pH value	6.0_ 9.0	6.0_ 9.0		5.0_ 9.0
Oil content_ mg/L	≤10	≤5		≤10
COD_ mg/L	≤100	≤60		≤20
Sulfide_ mg/L	≤1.0	≤1.0		≤1.0
Ammonia-nitrogen_ mg/L	≤15	≤15		≤10
Phenol_ mg/L	≤0.5	≤0.5		≤1
SS, mg/L	≤70	≤70		≤30
BOD5	≤30	≤20		≤20
Phosphate, mg/L	≤0.5	≤0.5		

APPENDIX (C.2)

G.B Standard for Petroleum Refinery WW treated effluent

No	Sample	Items	Specification	Frequency
1	Total oily water inlet	Oil content mg/L	< 800	1/24hr
		Volatilisation hydroxybenzene (phenol) mg/L	< 20	1/24hr
		COD mg/L	<800	1/24hr
		Ph	6—9	1/12hr
		Ammonia nitrogen mg/l	Report	1/24hr
		Sulfide mg/l	< 10	1/24hr
2	Oil separator out let	Oil content mg/l	< 150	1/24hr
3	Out of floating pools	Ph	6—9	1/12hr
		COD mg/L	< 150	1/12hr
		NH3-N mg/l	Report	1/24hr
		Oil content mg/l	< 10	1/12hr
4	Out let of biochemical pool C	SV	10—40	1/12hr
		MLSS	2—4	1/48hr
		SVI	80—150	2/week
		Lens check	Report	1/12hr
		BOD5 mg/l	< 30	1/week
		Dissolved oxygen mg/l	Report	1/12hr
		Ammonia nitrogen mg/L	Report	1/12hr
		Phosphate mg/l	Report	1/12hr
5	Out let of biochemical pool F	SV	10—40	1/12hr
		MLSS	2—4	1/48hr
		SVI	80—150	2/week
		BOD5 mg/l	< 30	1/week
		Dissolved oxygen mg/l	Report	1/12hr
		Lens check	Report	1/12hr
		Phosphate mg/l	Report	1/12hr
		Ammonia nitrogen mg/L	Report	1/12hr
6	P-3306	TSS mg/l	Report	1/12hr
7	Out let of monitoring monitoring pond	pH	5 ~ 8	1/24hr
		Oil content mg/L	≤ 10	1/24hr
		Sulfide mg/L	≤ 0.5	1/24hr
		COD mg/L	≤ 100	1/24hr
		BOD5 mg/L	≤ 30	1/week

		Volatilization hydroxybenzene (phenol) mg/L	≤ 0.5	1/48hr
		Ammonia nitrogen mg/L		1/24hr
		SS mg/L	≤ 70	1/48hr

APPENDIX (C.3)

Typical composition of some petroleum refinery wastewater effluent

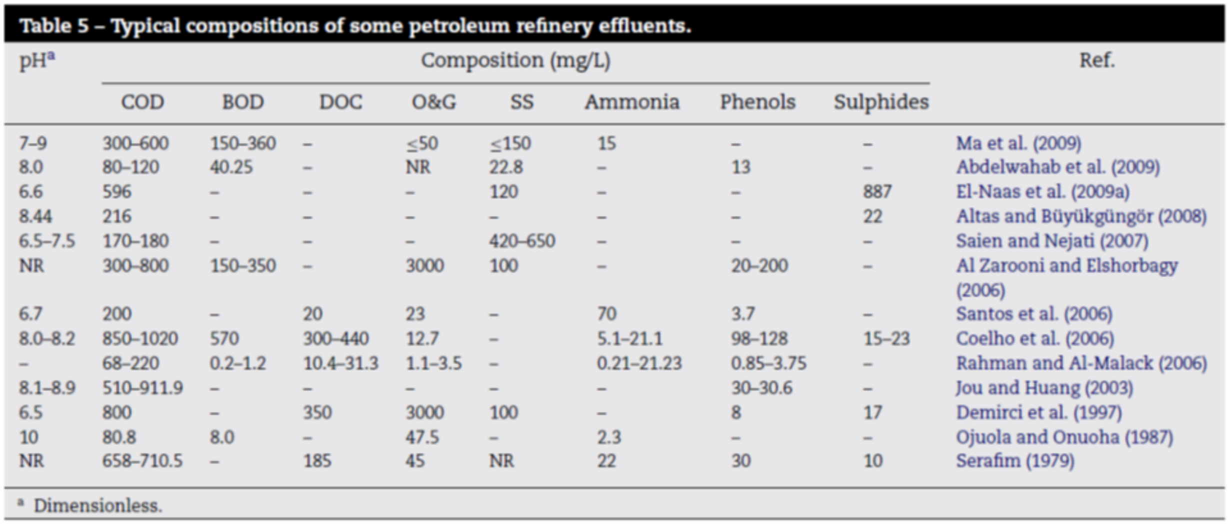


Table 5 – Typical compositions of some petroleum refinery effluents.

pH[a]	Composition (mg/L)								Ref.
	COD	BOD	DOC	O&G	SS	Ammonia	Phenols	Sulphides	
7–9	300–600	150–360	–	≤50	≤150	15	–	–	Ma et al. (2009)
8.0	80–120	40.25	–	NR	22.8	–	13	–	Abdelwahab et al. (2009)
6.6	596	–	–	–	120	–	–	887	El-Naas et al. (2009a)
8.44	216	–	–	–	–	–	–	22	Altas and Büyükgüngör (2008)
6.5–7.5	170–180	–	–	–	420–650	–	–	–	Saien and Nejati (2007)
NR	300–800	150–350	–	3000	100	–	20–200	–	Al Zarooni and Elshorbagy (2006)
6.7	200	–	20	23	–	70	3.7	–	Santos et al. (2006)
8.0–8.2	850–1020	570	300–440	12.7	–	5.1–21.1	98–128	15–23	Coelho et al. (2006)
–	68–220	0.2–1.2	10.4–31.3	1.1–3.5	–	0.21–21.23	0.85–3.75	–	Rahman and Al-Malack (2006)
8.1–8.9	510–911.9	–	–	–	–	–	30–30.6	–	Jou and Huang (2003)
6.5	800	–	350	3000	100	–	8	17	Demirci et al. (1997)
10	80.8	8.0	–	47.5	–	2.3	–	–	Ojuola and Onuoha (1987)
NR	658–710.5	–	185	45	NR	22	30	10	Serafim (1979)

[a] Dimensionless.