DESIGN OF A HYBRID INTEGRATED EFFLUENT TREATMENT SYSTEM FOR PETROLEUM REFINERY

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(with specialization in Industrial Pollution Abatement)

By

K. KIRAN KUMAR

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE -247 667 (INDIA)
JUNE, 2007

INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE
CANDIDATE'S DECLARATION

I declare that the work, which is being presented in the dissertation entitled **"DESIGN OF A HYBRID INTEGRATED EFFLUENT TREATMENT SYSTEM OF PETROLEUM REFINERY"**, in the partial fulfillment of the requirements of the award of the degree of Master of Technology in Chemical Engineering with specialization in Industrial Pollution Abatement, submitted in the Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand (India), is an authentic record of my own work carried out during the period from July 2006 to June 2007 under supervision of **Dr. I. D. Mall**, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, and **Mr. J. K. Joshi**, Senior Manager, Environment Division, Engineers India Limited, New Delhi, India.

I have not submitted the matter, embodied in this dissertation for the award of any other degree or diploma.

Date: 19 June 2007
Place: Roorkee

K. KIRAN KUMAR

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

(Dr. I. D. Mall)
Professor
Department of Chemical Engineering
IIT Roorkee,
Roorkee,
Uttarakhand, Pin - 247 667

(Mr. J. K. Joshi)
Senior Manager (Environment)
Engineers India Limited
Engineers India Bhavan
1, Bhikaji Cama Place,
New Delhi – 110 066, India

ACKNOWLEDGEMENT

I express my deep sense of gratitude to my guide **Dr. I. D. Mall**, Professor, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, for his keen interest, constant guidance and encouragement throughout the course of this work. Then, I would like to thank my co-advisor, Mr. Jayant Kumar Joshi, Senior Manager, Engineers India Limited, New Delhi for his continuous support in the M. Tech programme. He was always there to listen and to give advice and showed me different ways to approach wastewater plant design and the need to be persistent to accomplish any goal. Their experience, assiduity and deep insight of the subject held this work always on a smooth and steady course. Useful criticism and constant help extended in the hours of need had been immensely useful.

I am also thankful to **Mr. A. Haldar**, HOD, Environment Division, Engineers India Limited, New Delhi allowing me to do the thesis work in EIL.

Thanks are also due to **Dr. Shri Chand**, Professor and Head, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, for providing various facilities during this dissertation. A special thanks foes to all the personnel of Environment Division, Engineers India Limited, New Delhi for helping me and giving valuable suggestions during the course of my work.

I am greatly indebted to my friends Amritash, Anand, Chandrakant, Ravi, for their enthusiastic support, encouragement and help, made me come up with this report.

I thank all well wishers who in any manner directly or indirectly have put a helping hand in this piece of work.

Above all, I want to express my heartiest gratitude to all my family members for their love, faith and support for me, which has always been a constant source of inspiration.

K. Kiran Kumar

ABSTRACT

Rapid industrialization, unplanned urban development, increasing automobile emission has resulted in serious environmental degradation. To defend and to improve environment for present and future generations by making industrial plants healthier and more pleasant to work, mitigating impact of industrialization by eco-friendly greener technologies, preserving ecological balance has become an imperative goal of mankind. Petroleum refineries are typically large sprawling industrial complex and are critical to functioning of the economy.

Petroleum refineries use large quantity of water and steam in a variety of processes and approximately 3.5 – 5 m^3 of wastewater from processing units are generated per ton of crude processed in a typical refinery containing oil and grease, BOD, phenols, COD, toxicity, pH, suspended solids, ammoniacal nitrogen, sulphides, TDS, cyanides, etc. In the existing wastewater treatment (WWT) system, refineries generally use trickling filters in combination with activated sludge process as a secondary treatment system. The use of sequencing batch reactors (SBR), membrane bioreactors (MBR) and reverse osmosis skids have received considerable interest during recent years to overcome the weakness of existing biological treatment system.

As the concept of "Zero liquid discharge" has emerged in petroleum refineries so as to obtain all norms required by the regulatory boards, a hybrid integrated effluent treatment system for petroleum refinery has become need of time. The objective of present work is to design a hybrid integrated effluent treatment system to have the zero discharge with demineralized (DM) water parameters for the treated effluent. In the present work flow scheme, process description; process flow diagrams (PFD) of integrated petroleum refinery; refinery effluents and possible choices for their treatment; existing wastewater treatment system; and new hybrid integrated effluent treatment system has been presented to meet the requirement of zero discharge and compliance of regulatory parameters. Detailed design of individual units (viz. API, TPI, DAF, SBR, MBR and RO Skid) and equipments, plant lay out is presented in this dissertation report. As SBR is new to refinery wastewater, studies on the impact of temperature on various parameters [viz. SRT, AOUTR, oxygen required, overall yield, etc.] have been presented. Finally, cost estimation has also been done for setting up such a hybrid integrated effluent treatment system.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

NOMENCLATURE

μ	Absolute viscosity of wastewater, *cP*
g	Acceleration due to gravity, m/sec^2
V_T	Vertical velocity/rise rate of design oil globule, *m/sec*
ρ_w	Density of water, Kg/m^3
ρ_o	Density of oil, Kg/m^3
D_P	Diameter of oil globule which is to be separated or removed, *m*
A_C	Minimum vertical cross – sectional area, m^2
n	Number of separator channels
B	Channel width, *m*
L	Length of the separator, *m*
F	Turbulence and short – circuiting factor
V_H	Horizontal velocity, *m/sec*
d	Depth of channel, *m*
A_P	Projected surface area of the plates, m^2
A_A	Actual Plate area, m^2
υ	Kinematic viscosity, m^2/sec
Re	Reynolds number
N_P	Number of plates
S	Mass of solids, *mg*
s'_a	Solubility in air, *mL/L*
S_I	Influent suspended solids, *mg/L*
Q	Mixed liquor flow, m^3/hr
f	Fraction of air dissolved at pressure P, *atm*
P	Operating temperature, *atm*
A_r	Surface area, m^2
SLR	Surface loading rate, gpm/ft^2
V_T	Total volume, m^3
V_S	Settled volume after decant, m^3

$\mathbf{X_T}$	MLSS concentration at full volume, *g/m³*
$\mathbf{X_S}$	MLSS concentration in settled volume, *g/m³*
$\mathbf{K_{dn}}$	Endogenous decay coefficient, *g VSS/(g VSS * day)*
TSS	Total suspended solid, *g/m³*
MLSS	Mixed liquor suspended solids, *g/m³*
MLVSS	Mixed liquor volatile suspended solids, *g/m³*
$\boldsymbol{\tau}$	Hydraulic retention time, *hr*
$\mathbf{L_{ORG}}$	BOD volumetric loading, $Kg/(m^2 * hr)$
$\mathbf{f_D}$	Cell Debris, *g/g*
$\mathbf{R_O}$	Oxygen required, *Kg/day*
$\mathbf{P_{X,BIO}}$	Biomass as VSS wasted/day, *Kg/day*
AOUTR	Average oxygen uptake transfer rate, *Kg/hr*
$\mathbf{X_N}$	Nitrifier concentration, g/m^3
$\mathbf{K_O}$	Half-saturation constant for DO, g/m^3
SRT	Solid retention time, *days*
TKN	Total Kjeldahl Nitrogen, g/m^3

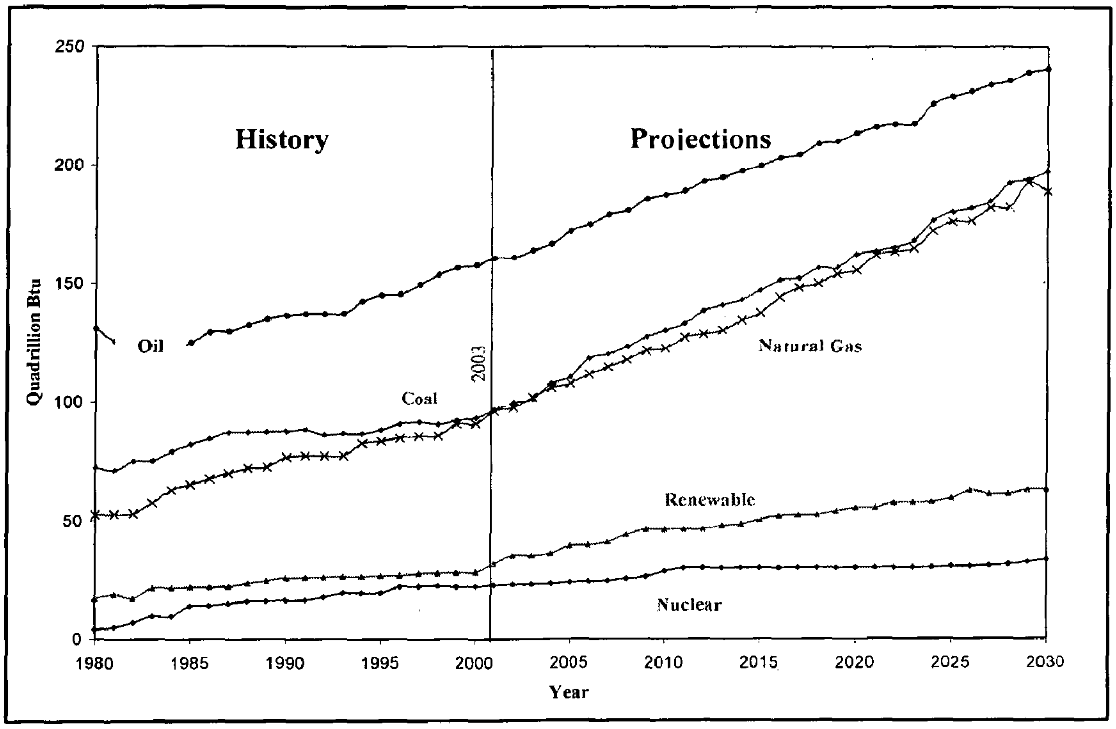
CHAPTER 1

INTRODUCTION

Energy is known to play a vital role in the industrial and economic development of any country and it's true that petroleum refineries have revolutionized our life and are providing the major basic needs of rapidly growing source of energy for domestic, industrial, transport sectors; and as feedstock for fertilizers, synthetic fibers, synthetic rubbers, polymers, intermediates, explosives, dyes, paints, etc. Globally it processes more material than any other industry [Mall, 2006]. The petroleum refineries processes crude oil and produces a variety of products that are used in transportation, residential, commercial, and industrial sectors of economy. Virtually all transportation, land, sea, and air are fueled by products that are refined from crude oil. Petroleum refineries are typically large sprawling industrial complexes with extensive piping running throughout, carrying streams of fluid between large chemical processing units [Pirog, 2007].

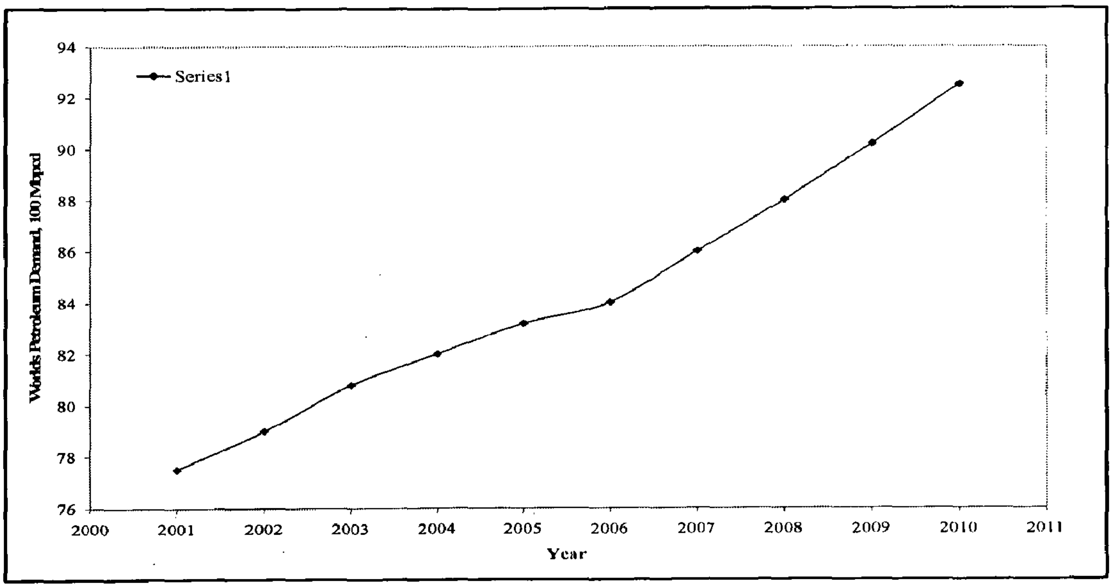
1.1 PROFILE OF PETROLEUM REFINING INDUSTRY

As per history, the first oil wells were drilled in China in the fourth century or earlier. They had depths of up to 243 *m* and were drilled using bits attached to bamboo poles. From there onwards the refining industry never looked back and the modern history of petroleum began in 1846, with the discovery of refining kerosene from coal.. The American petroleum industry began with Edwin Drake's drilling of 69-*feet*-deep oil well in 1859, near Titusville, Pennsylvania. In 2006, over two-thirds of the refinery output went to transportation uses, nearly a quarter went to industrial uses, and remainder was used in residences, commercial activities, and electricity generation. Figure 1 uses information from US Energy Information Agency (EIA) and illustrates worlds market energy use by energy type of various fuels in between the years 1980 and 2030. The current petroleum demands were exploited using the growth rates mentioned. Figure 2 summarizes the petroleum demand forecast through 2010. The primary drivers for this growth are economic and demographic [Goyal, 2006].



[**Source:** **History:** Energy Information Administration (EIA), International Energy Annual, 2003 (May – July 2005), website: www.eia.doe.gov/iea; Projections: EIA, System for Analysis of Global Energy Markets (2006)]

Figure 1: World Marketed Energy Use by Energy Type, 1980 – 2030.

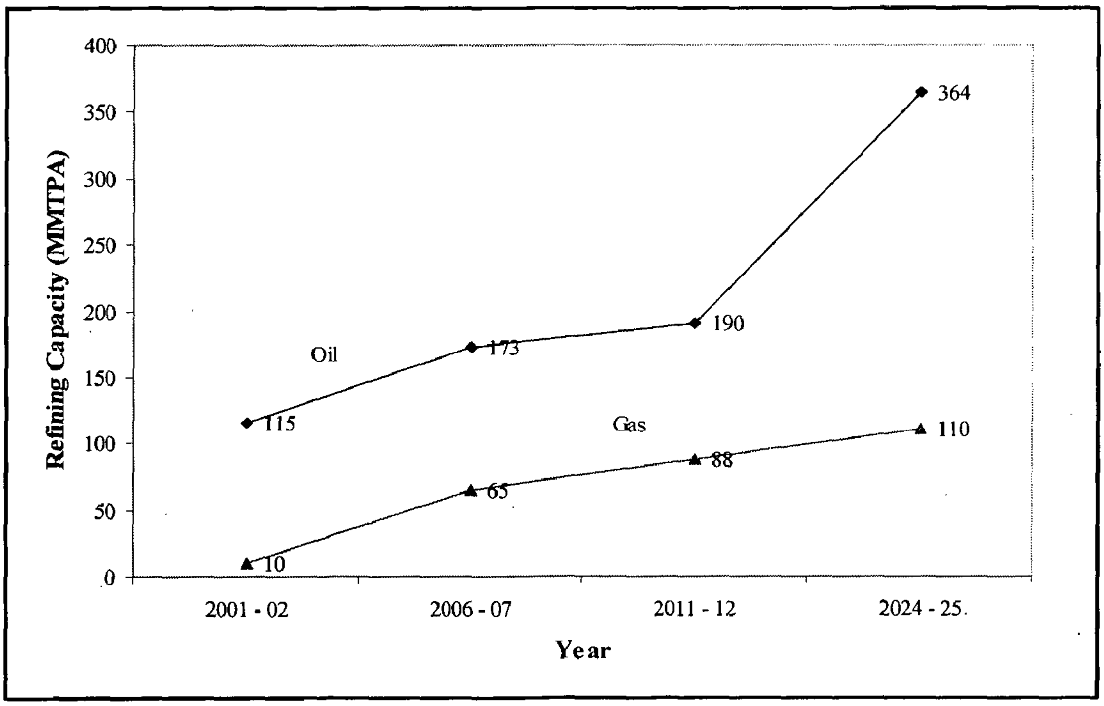


[**Source:** Goyal, 2006]

Figure 2: Forecast of World Petroleum Demand.

1.2 THE INDIAN PETROLEUM REFINING SECTOR

The Indian petroleum industry is one of the oldest in the world; oil having been struck at Makum, near Margheritta in upper Assam in 1867 [Singh, 2002]. The Indian oil refining sector has 10 companies with 19 refiners and combined installed capacity of over 146 MMTPA [Chemical Industry Digest, 2007]. Of these companies, RIL is a private sector company, MRPL a joint sector entity and the rest public sector enterprises. ONGC is recent entrant in the refining business and has taken a stake is MRPL [An energy overview of India, 2003]. Demand for petroleum products in the country is estimated to reach 370 MMTPA by 2025. India Hydrocarbon Vision – 2025 contemplates a crude processing capacity of 395 MMTPA at an investment of about $ 60 billion, and another 10% for infrastructure, raising the existing storage capacity from 14 million KL to 34 million KL. With the Reliance plan materializing an announced and the ongoing projects fructifying, India would touch the ball park figure of 250 MMTPA by 2011 – 12. Figure 3 represents oil and gas demand in coming future [Goyal, 2006].



[**Source:** Hydrocarbon Vision, 2025]

Figure 3: Oil & Gas – Demand in Future.

1.3 PROCESS TECHNOLOGY

Petroleum refining is the physical, thermal, and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished petroleum products. The primary products of the industry fall into three major categories: fuels (motor gasoline, diesel, distillate, fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke); finished non-fuel products (solvents, lubricating oil, greases, petroleum wax, petroleum jelly, asphalt, and coke); and chemical industry feedstocks (naphtha, ethane, propane, butane, ethylene, propylene, butylenes, butadiene, benzene, xylene, and toluene). These petroleum products are used as primary input to vast number of products, including fertilizers, pesticides, paints, waxes, thinners, solvents, cleaning fluids, detergents, refrigerants, antifreeze, resins, sealants, insulations, latex, rubber compounds, detergents, hard plastics, plastic sheeting, plastic foam, and synthetic fibers [Leffler, 1985]. The overview of petroleum refining processes is mentioned in Table 1. As the new standards for products are becoming stricter in terms of sulphur content, more and more product sweetening processes are in anvil. More demand for middle distillate has also been given a boost to cracking, isomerization, alkylation, and delayed coking units as the demand for the fuel oil is on decline.

1.4 ENVIRONMENTAL POLLUTION IN PETROLEUM REFINING AND TREATMENT TECHNOLOGY

Petroleum refineries use and generate an enormous number of chemicals, many of which leave the facilities as discharge of air emissions, wastewater or solid waste. Pollutants generated typically include VOCs, carbon monoxide (CO), sulphur oxides (SO_X), nitrogen oxides (NO_X), particulates, ammonia (NH_3), hydrogen sulphide (H_2S), metals, spent acids, and numerous toxic compounds. Figure 4 summarizes the main pollutants output from each unit of a petroleum refinery.

Table 1: Overview of Petroleum Refining Processes

Process Name	Action	Method	Purpose	Feedstock (s)	Products
Fractionation process					
Atmospheric distillation (1862)	Separation	Thermal	Separate fractions	Desalted crude oil	Gas, gas oil, distillate, residual
Vacuum distillation (1870)	Separation	Thermal	Separate w/o cracking	Atmospheric tower residual	Gas oil, lube stock, residual
Conversion processed – Decomposition					
Catalytic cracking (1937)	Alteration	Catalytic	Upgrade gasoline	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Coking (1932)	Polymerize	Thermal	Convert vacuum residuals	Gas oil, coke distillate	Gasoline, petrochemical feedstock
Hydro-cracking (1960)	Hydrogenate	Catalytic	Convert to lighter hydrocarbons	Gas oil, cracked oil, residuals	Lighter, higher-quality products
Hydrogen steam-reforming	Decompose	Thermal/ Catalytic	Produce hydrogen	Desulphurized gas, oxygen, steam	Hydrogen, carbon monoxide, carbon dioxide
Steam cracking	Decompose	Thermal	Crack large molecules	Atmospheric tower heavy fuel/distillate	Cracked, naphtha, coke, residual
Visbreaking (1939)	Decompose	Thermal	Reduce viscosity	Atmospheric tower residual	Distillate, tar
Conversion processed – Alteration or Rearrangement					
Catalytic reforming (1952)	Alteration/ dehydration	Catalytic	Upgrade low-octane naphtha	Coker/hydro-cracker naphtha	High octane reformate/ aromatics
Isomerization (1940)	Rearrange	Catalytic	Convert straight chain to branch	Butane, pentane, hexane	Isobutane, pentane, hexane
Conversion processed – Unification					
Alkylation (1940)	Combining	Catalytic	Unite olefins and iso-paraffins	Tower iso-butane/cracker olefins	Iso-octane (alkylate)

Table 1: Overview of Petroleum Refining Processes (Contd.)

Grease compounding	Combining	Thermal	Combine soaps & oils	Lube oil, fatty acids, alkylated metal	Lubricating grease
Polymerizing (1935)	Polymerize	Catalytic	Unite two or more olefins	Cracker olefins	High-octane naphtha, petrochemical feedstock
Treatment processes					
Amine treating	Treatment	Absorption	Remove acidic components	Sour gas, hydrocarbons, wet CO_2, H_2S	Acid free gas and liquid hydrocarbons
Desalting	Dehydration	Absorption	Remove salts of Ca, Mg, Na, etc.	Crude oil	Desalted crude oil
Drying and sweetening (1956)	Treatment	Absorption/ Thermal	Remove water and sulphur compounds	Liquid hydrocarbons, LPG, alkylated feedstock	Sweet and dry hydrocarbons
Furfural extraction	Solvent extraction	Absorption	Upgrade mid distillate and lubes	Cycle oils and lube feed stocks	High quality diesel and lube oil
Hydrodesulphurization (1954)	Treatment	Catalytic	Remove sulphur, contaminants	High sulphur residual/gas oil	Desulphurized olefins
Hydrotreating	Hydrogenation	Catalytic	Remove sulphur, saturate hydrocarbons	Residuals, cracked hydrocarbons	Cracker feed, distillate, lube
Phenol extraction	Solvent extraction	Absorption/ Thermal	Improve viscous index, colour	Lube oil base stocks	High quality lube oils
Solvent deasphalting (1950)	Treatment	Absorption	Remove asphalt	Vacuum tower residual, propane	Heavy lube oil, asphalt
Solvent dewaxing (1935)	Treatment	Cool/filter	Remove wax from lube stocks	Vacuum tower lube oils	Dewaxed lube base stocks
Solvent extraction (1933)	Solvent extraction	Absorption/ precipitation	Separate unsaturated oils	Gas oil, reformate, distillate	High-octane gasoline
Sweetening (1916)	Treatment	Catalytic	Remove H_2S, convert mercaptans	Untreated distillate/ gasoline	High-quality distillate/ gasoline

[**Source:** *http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html*]

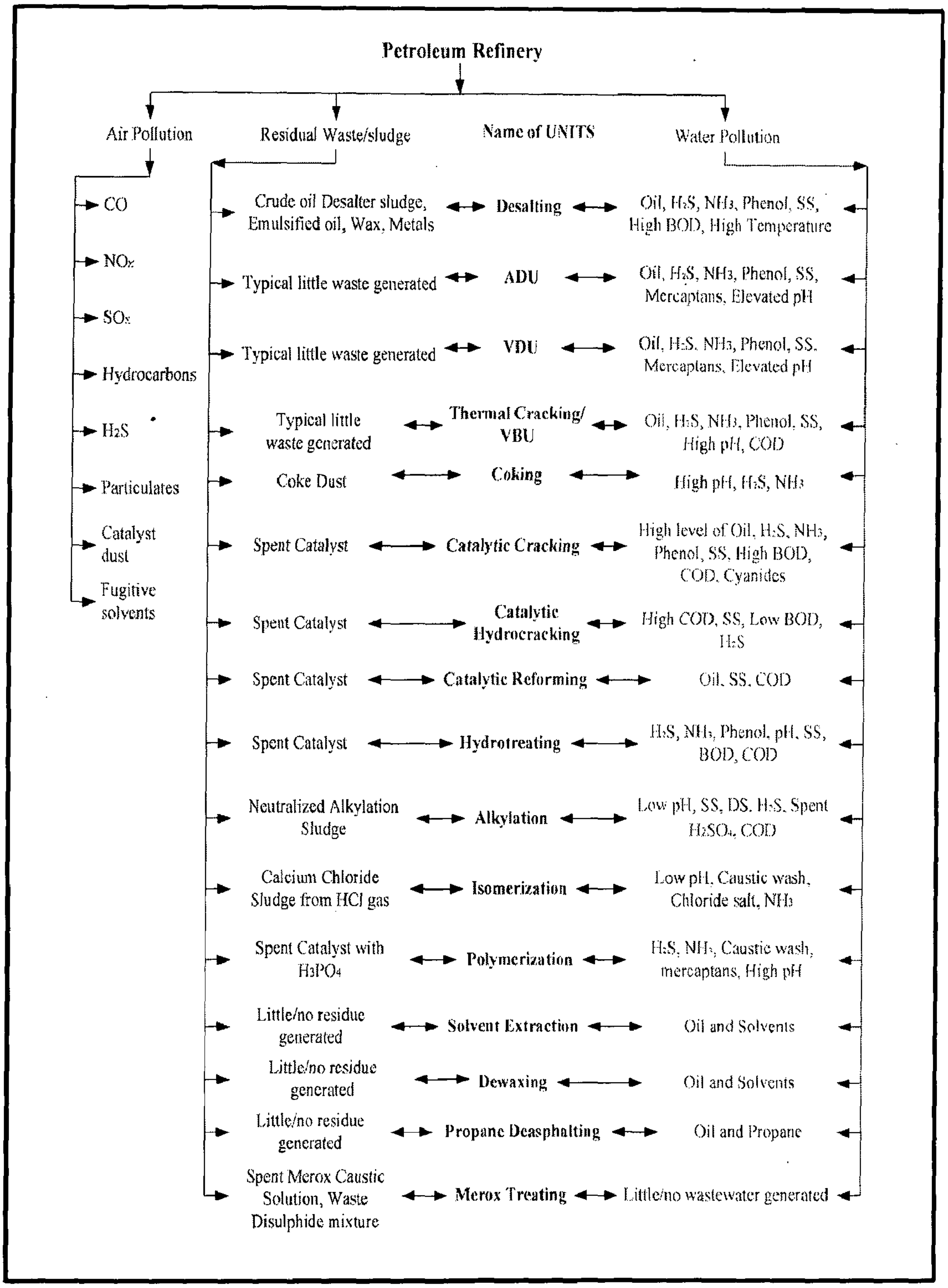


Figure 4: Major Pollution (Air, Water, & Soil) Caused by a Petroleum Refinery.

1.5 WASTEWATER TREATMENT TECHNOLOGY AND FUTURE SCENARIO

Relatively large amount of water are used by the petroleum refinery industry. Petroleum refineries typically utilize primary and secondary wastewater treatment. Primary wastewater treatment system consists of the separation of oil and solids in two stages. During the first stage, an API separator, a corrugated plate interceptor or other separator is used. Wastewater moves very slowly through the separator allowing free oil to float to the surface and be skimmed of and solids to settle at the bottom and be scrapped of to a sludge collecting hopper. The second stage utilizes physical or chemical methods to separate emulsified oils from the wastewater. Physical methods may include the use of series of settling ponds with a retention time or the use of dissolved air flotation (DAF). Chemicals such as ferric hydroxide or aluminium hydroxide can be used to coagulate impurities into a froth or sludge which can be more easily skimmed off from the top. In some countries, after primary treatment the wastewater can be discharged to a publicly owned treatment works or secondary treatment before being discharged directly to surface waters. In secondary treatment, dissolved oil and other organic pollutants may be consumed biologically by micro-organisms. Biological treatment may require the addition of oxygen through a number of different techniques including activated sludge units, trickling filters, aerated lagoons, oxidation ponds, and rotating biological contactors. Secondary treatment generates bio-mass waste which is typically treated anaerobically and then dewatered. After biological treatment additional stage of wastewater treatment is put up for polishing of treated wastewater in order to meet discharge limits. The polishing step can involve the use of activated carbon, anthracite coal or sand to filter out any remaining impurities such as biomass, silt, trace metals, and other inorganic chemicals, as well as any remaining organic chemicals. The treated wastewater is chlorinated before discharging to surface drain and is recycled/reused for different purpose such as horticulture, equipment washing, floor washing or in some cases make up water for cooling tower. The concept of "Zero liquid discharge" has emerged in the industry and all modern treatment processes are aimed to achieve the same.

The use of sequencing batch reactors (SBR), membrane bio-reactors (MBR) and reverse osmosis (RO) skid are playing a very important role now a day in wastewater treatment. Future work is on the design of these reactors and by studying the pilot plant data and implementation in the site of refineries as wastewater treatment scheme (as secondary and tertiary treatment scheme). The detailed description of petroleum refining industry and advanced wastewater treatment in petroleum refineries is mentioned in next chapters.

1.6 OBJECTIVE

The theme of this dissertation report is to "Design of a hybrid integrated effluent treatment for petroleum refinery" for reuse and recycle of water as demineralized (DM) water make up and to maintain all norms required by the regulatory boards, based on effluent quality, effluent quality standards, and design criteria are given in Table 2, 3, and 4, respectively.

Table 2: Wastewater Quality Parameters (Oily Effluent Flow: 300 m^3/hr)

Parameters	**Concentration**
Temperature (^{O}C)	25
pH	5.5 – 9.0
Oil	1000 – 20000
Total Suspended Solids	200
BOD	1000
COD	1700
Total Sulphides (as S)	235
Phenols	100
Ammonia (as NH_3)	50
Total Dissolved Solids	5000
Organophosphate as PO_4, *mg/L*	10
Conductivity, *micro mho/cm*	9000
M Alkalinity as $CaCO_3$, *mg/L*	2000
Calcium Hardness as $CaCO_3$, *mg/L*	190
Magnesium Hardness as $CaCO_3$, *mg/L*	530
Sodium + Potassium as $CaCO_3$, *mg/L*	2380
Chlorides as Cl, *mg/L*	300
Sulphates (as SO_4), *mg/L*	830
Phosphates + Nitrate (as $PO_4 + NO_3$), *mg/L*	78
Ammonia as NH_3, *mg/L*	90
Iron as Fe, *mg/L*	1.0
Total Silica as SiO_2, *mg/L*	25
Reactive Silica as SiO_2, *mg/L*	22.5
SDI	Out of range
$KMnO_4$ consumption at $37^{O}C$	10
All Other Metals	Traces

Table 3: Demineralized (DM) Water Parameters

Parameter	Limiting value for concentration
pH	6.7 – 7.3
Turbidity	Nil
Total hardness as $CaCO_3$, (in *ppm*)	Nil
Conductivity @$25^{o}C$, in *micro mho/cm*	<0.2
Reactive silica as SiO_2 (in *ppm*)	<0.01
Copper (in *ppm*)	<0.003
$KMnO_4$ value @ $100^{o}C$ (in *ppm*)	<5
Oil content (in *ppm*)	Nil
Na + K as $CaCO_3$ (in *ppm*)	<0.01
Total dissolved solids (in *ppm*)	<0.1
Total chlorides as Cl (in *ppm*)	Nil
Total iron as Fe (in *ppm*)	<0.01

Table 4: Basic Design Criteria

Inorder to design a hybrid integrated effluent treatment system for a petroleum refinery so as to meet the stringent standards of DM water quality, the following steps are to be done:

1. Removal of free oil by using an API and TPI system.
2. Removal of emulsified oil by using the systems, such as DAF/CAF/DGF system.
3. Removal of sulphides by making use of Wet air oxidation/$FeCl_3$ oxidation/H_2O_2 oxidation.
4. Two stage biological treatments includes: Biotower/Extended aeration/SBR/MBR, etc.).
5. Polishing system (Sand filtration/Activated carbon adsorption).

If reuse plant is to be designed then,

1. Basket filtration followed by Ultra filtration.
2. Cartridge filtration followed by Reverse Osmosis (RO).

If DM quality water is desired

1. Mixed bed polishing (Resin based treatment).

1.7 EFFLUENTS AND EMISSION STANDARDS

The various parameters for the discharge effluents which are to be considered are mentioned in Table 5, 6 (a) and 6 (b) respectively, which are given below:

Table 5: Minimal National standards (MINAS) for Discharge Effluents in Petroleum Refineries

S No.	Parameter	Limiting value for concentration (*mg/L*, except for pH)	Limiting value for quantum (*kg/1000 Tonnes* of crude processed, except for pH)	Averaging Period
Parameters to be monitored daily: Grab samples for each shift with 8 - *hours'* interval				
1	pH	6.0 – 8.5	-	Grab
2	Oil & Grease	5	2	-do-
Parameters to be monitored daily: Composite sample (with 8 - *hours'* interval) for *24 - hours* flow weighted average				
3	$BOD_{3\ days,\ 27^{O}C}$	15	6	24 - *hours*
4	COD	125	50	-do-
5	Suspended Solids	20	8	-do-
6	Phenols	0.35	0.14	-do-
7	Sulphides	0.5	0.2	-do-
8	CN	0.2	0.08	-do-
Parameters to monitored once in a month: composite sample (with 8 - *hours'* interval) for 24 - *hours* flow weighted average				
9	Ammonia as N	15	6	-do-
10	Total Kjeldahl Nitrogen (TKN)	40	16	-do-
11	P	3	1.2	-do-
12	Cr (VI)	0.1	0.04	-do-
13	Total Cr	2.0	0.8	-do-
14	Pb	0.1	0.04	-do-
15	Hg	0.01	0.004	-do-
16	Zn	5.0	2	-do-
17	Ni	1.0	0.4	-do-
18	Cu	1.0	0.4	-do-
19	V	0.2	0.8	-do-
Parameters to monitored once in a month: grab samples for each shift with 8 - *hours'* interval				
20	Benzene	0.1	0.04	Grab
21	Benzo(a) pyrene	0.2	0.08	-do-

Table 6 (a): Ambient Air Noise Standards in Petroleum Refineries (Category Wise)

Area Code	Category of Area	Limits (in dB_A), L_{eq}	
		Day time	Night Time
A	Industrial Area	75	70
B	Commercial area	65	55
C	Residential area	55	45
D	Silence zone	50	40

Table 6 (b): Ambient Air Noise Standards in Petroleum Refineries

Exposure Time, *hrs/day*	Limit (in dB_A), L_{eq}
8	90
4	93
2	96
1	99
$\frac{1}{2}$	102
$\frac{1}{4}$	105
$\frac{1}{8}$	111
$\frac{1}{16}$	114

CHAPTER 2

PETROLEUM REFINING PROCESSES

Raw oil or unprocessed (crude) oil is not very useful in the form it comes out of the ground as crude oil is a mixture of different hydrocarbons and small amount of impurities. Petroleum refineries are a complex system of multiple operations and the operations used at the refinery depend upon the properties of crude oil to be refined and the desired products. The major unit operations typically involved in petroleum refineries is discussed below. Refining crude oil into crude petroleum products can be separated into two phases and a number of supporting operations. The first phase is desalting of crude oil and the subsequent distillation into its various components or fractions. The second phase is made up of three different types of downstream processes: combining, breaking, and reshaping. Downstream processes convert some of the distillation fractions into petroleum products (residual fuel oil, gasoline, kerosene, etc.) through any combination of different cracking, coking, reforming, and alkylation processes. Refining technology has evolved considerably over the last century – largely in response to changing product requirements: gasoline for automobile, petrochemical as building block for clothing and consumer goods, and more environmental friendly processes and products [Katzer et al., 2000]. Supporting operations may include wastewater treatment, sulphur recovery, additive production, heat exchanger cleaning, blowdown system, blending of products, and storage of products.

2.1 CRUDE OIL DISTILLATION AND DESALTING [Gary & Handwerk, 1994; Mall, 2006; Petroleum Refinery Enforcement Manual, 1980; Ram Prasad, 2000; Stutz, 1972]

One of the most important operations in a refinery is the initial distillation of crude oil into its boiling point fractions. Distillation involves heating, vapourization, fractionation, condensation, and cooling of feedstock. This section also discusses the atmospheric and vacuum distillation processes and the important step of desalting the crude oil prior to distillation.

2.1.1 Desalting

Crude oil often contains water, inorganic salts, suspended solids, and water-soluble trace metals. To reduce corrosion, plugging, fouling of equipments, and to prevent poisoning of the catalysts in the processing units, these contaminants must be removed by desalting. Desalting involves the mixing of heated crude oil with low TDS water (about 3 – 10% of crude oil volume) so that the entrapped salts in the crude are dissolved in the water. Desalting process consists of three stages: heating, mixing, and settling and two phase water/oil layer is separated by using demulsifying chemicals to break down the emulsion or by passing high potential electric current (~ 20000 *V*).

2.1.2 Atmospheric Distillation

The desalted crude oil is then heated in a heat exchanger and in furnace to about $400^{O}C$ and fed to vertical, distillation column at atmospheric pressure where most of the feed is vapourized and separated into various fractions by condensing on fractionation trays, each corresponding to different condensation temperature. The lighter fractions condense and are collected towards the top of the column. Some of the heavier fractions can be converted to lighter fractions by introducing steam from the bottom of the distillation column. Function of the steam is to reduce the partial pressure of the hydrocarbons. Heavier fractions, which may not vaporize in the column, are further separated by vacuum distillation. Fractions obtained from atmospheric distillation include LPG, naphtha, gasoline, kerosene, light fuel oil, diesel oil, gas oil, lube distillate, and heavy bottoms. The process conditions are here under:

	Distillation column	
	Top	**Flash**
Temperature (^{O}C)	117 – 123	351 – 357
Pressure (kg/cm^2)	2.2 – 2.5	2.5 – 2.9

2.1.3 Vacuum Distillation

It is distillation of the residue of atmospheric distillation column carried out to make it suitable for catalytic cracking or hydrocracking or manufacturing of lubricating oil and a residue which may be air blown or further distilled for bitumen. To avoid cracking of atmospheric residue, which requires high temperature; distillation of the residue is carried out under vacuum. This permits the fractionation at low temperature. The process conditions are here under:

	Distillation Column	
	Top	**Flash**
Temperature (^{O}C)	70 – 80	390 – 395
Pressure (*mm of Hg*)	70 – 90	130 – 150

2.2 Downstream Processing

Downstream processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher molecules. These downstream processes include: thermal cracking (visbreaking), coking, catalytic cracking, catalytic hydrocracking, hydrotreating, alkylation, isomerization, polymerization, catalytic reforming, solvent extraction, merox extraction, dewaxing, propane deasphalting, and various other operations.

2.2.1 Thermal Cracking

Thermal cracking can include visbreaking and coking, in addition to regular thermal cracking. Heavy gas oil fractions are broken down into lower molecular weight fractions such as domestic heating oils, residue from vacuum distillation process, catalytic cracking stock, and other fractions by heating, but without the use of catalyst. The feedstock is heated in furnace in between 480 – 600^{O}C and then fed to a reaction chamber which is kept at a pressure of 41.6 – 69.1 *atm*. The product is then fed to flash chamber, where the pressure is reduced and lighter products vapourize and drawn off and are finally separated in fractionating tower. The bottom consists of heavy residue, part of which is recycled to cool the process stream leaving reaction chamber, the remaining bottoms are usually blended into residual fuel.

2.2.2 Coking

Coking is a severe method of thermal cracking used to upgrade low value residual fuel oils to transportation oils (such as gasoline, diesel, etc.). The process so completely reduces hydrogen that the residue is a form of carbon called “coke”. The two most common processes are delayed coking and continuous (fluid) coking. Three types of coke (viz. sponge coke, honeycomb coke, and needle coke) are obtained depending upon reaction mechanism, time, temperature, and crude feedstock.

2.2.3 Catalytic Cracking

Catalytic cracking breaks complex hydrocarbons into simpler molecules inorder to increase the quality and quantity of lighter, more desirable products, and decrease the amount of residuals. Feedstocks are light and heavy oils (from ADU), which are processed into lighter fractions such as kerosene, gasoline, LPG, heating oil, and petrochemical feedstock. Typical operating conditions are 450 – $510^{O}C$ and 0.65 – 1.5 *atm*. The catalysts used in these units are typically solid materials (zeolite, aluminium hydrosilicate, treated bentonite clay, fuller earth, and bauxite) that come in the form of powders, beads, pellets, etc. The catalytic cracking produces coke which collects on the catalyst surface and diminishes the catalyst properties. The catalyst therefore, needs to be regenerated continuously/periodically essentially by burning the coke off the catalyst at higher temperature. The fluidized and moving-bed are the most prevalent in recent years.

2.2.4 Catalytic Hydrocracking

Feedstock to hydrocracking units are often those fractions that are more difficult to crack and cannot be cracked effectively in catalytic cracking units. These include: middle distillate, cycle oil, residual fuel oil, and reduced crudes. This process converts these feedstocks into gasoline, high octane isoparaffins, jet fuels, diesel fuels, low-pressure gas, and low sulphur fuel oil. The operating conditions ranges in between 205 – $428^{O}C$ and 6.8 – 140 *atm*. Depending upon the products desired and the size of unit, catalytic hydrocracking is carried in either single-stage or multi-stage processes.

2.2.5 Hydrotreating/Hydroprocessing

Hydrotreating and hydroprocessing are similar processes used to remove impurities such as sulphur, nitrogen, oxygen, and trace metal impurities that may deactivate process catalyst. Hydrotreating also upgrades the quality of fractions by converting olefins and diolefins to paraffins for the purpose of reducing gum formation in fuels. Hydroprocessing, which typically uses residuals from crude distillation units, also cracks these heavier molecules to lighter more saleable products. Both these processes are placed upstream of those processes in which sulphur and nitrogen could have adverse effects on catalyst, such as catalytic reforming and hydrocracking units.

2.2.6 Alkylation

Alkylation is the reaction of an isoparaffins (usually isobutane) and an olefin (propylene, butylenes, amylenes) [formed during catalytic cracking and coking operations; but also from catalytic reforming, crude distillation, and natural gas processing] in the presence of a catalyst at carefully controlled temperatures and pressures to produce high-octane alkylate for use as a gasoline blending component. Propane and butane are also produced. Alkylation process occur in presence of a catalyst and various catalyst used in the process such as Lewis acid ($AlCl_3$), H_2SO_4, and HF, of which sulphuric acid is the most widely used catalyst. The reactor products are separated in a catalyst recovery unit from which the catalyst is recycled.

2.2.7 Isomerization

Isomerization is a process technique for converting light gasoline stocks (typically C_4H_{10} and C_5H_{12} from CDU) to high-octane isomers. It is used to alter the arrangement of molecule without adding or removing anything from original molecule. Isomerization reactions take place at a temperature in the range of $94 - 205^{O}C$ in the presence of catalyst that usually consists of platinum as base material. Two types of catalyst are in use and both types require an atmosphere of hydrogen to minimize coke deposits; however, the consumption of hydrogen is negligible. Light ends are stripped from the product stream leaving the reactor and are then sent to sour gas treatment unit.

2.2.8 Polymerization

Polymerization units convert olefin feedstocks (primarily propylene and butene) into higher octane polymers. The process is similar to alkylation in its feed and products, but is often used as an alternative to alkylation. The operating conditions are $150 - 224^{O}C$ and at a pressure of $11.2 - 137\ atm$ in presence of H_3PO_4 catalyst, although sulphuric acid is used in some older methods. These units consist of a feed treatment unit (to remove H_2S, mercaptans, and nitrogen compounds), a catalytic reactor, an acid removal section, and a gas stabilizer. The reaction products leaving the reactor are sent to stabilization and/or fractionator systems to separate saturated and unreacted gases from the polymer gasoline product.

2.2.9 Catalytic Reforming

Catalytic reforming is an important process used to convert low-octane naphthas into high-octane gasoline blending components called “reformates”. Reforming represents the total effect of numerous reactions such as cracking, polymerization, dehydrogenation, isomerization taking place simultaneously. Depending on the properties of naphtha feedstock and catalyst used, reformates can be produced with very high concentrations of toluene, benzene, xylene, and other aromatics useful in gasoline blending and petrochemical processing. Feedstock to catalytic reforming processes is usually hydrotreated first to remove sulphur, nitrogen, and metallic constituents.

2.2.10 Solvent Extraction

The purpose of solvent extraction is to prevent corrosion, protect catalyst in subsequent processes, remove aromatics from lube oil feedstocks, improving viscosity, oxidation resistance, colour, and gum formation and improve finished products by removing unsaturated, aromatic hydrocarbons from lubricants and grease stocks. A number of different solvent are used with the two most common being furfural and phenol. Solvents are recovered from the oil stream through distillation and steam stripping in a fractionator. The stream extracted from the solvent will likely contain high concentrations of H_2S, aromatics, naphthenes, and other hydrocarbons, and is often fed to hydrocracking unit.

2.2.11 Dewaxing

Dewaxing is a process of removing wax from lube oil, generally after deasphalting and solvent extraction so as to produce lubricants with low pour point and to recover wax for further processing. The wax is either used as a feed to catalytic cracker or is deoiled and sold as industrial wax.

2.2.12 Propane Deasphalting

Deasphalting is a solvent extraction process for removing asphalt or resins from viscous hydrocarbons to produce feedstocks for lube oil refining or catalytic cracking processes. Propane is usually used to remove asphaltenes due to its unique solvent properties.

2.2.13 Drying and Sweetening

Drying and sweetening is a broad class of processes used to remove sulphur compounds, water and other impurities from gasoline, kerosene, jet fuels, domestic heating oils, and other middle distillate products. Sweetening is the removal of hydrogen sulphide, mercaptans and thiophenes, which impart a foul colour and decrease the tetraethyl lead susceptibility of gasoline. Drying is accomplished by salt filters or absorptive clay beds. Electric fields are sometimes used to facilitate separation of product.

2.2.14 Merox Extraction

This process is used for removal of mercaptans or for conversion of mercaptans into disulphide. The process is combination of mercaptans extraction and sweetening. Low molecular weight mercaptans are caustic soluble and are removed by washing with caustic. The caustic is regenerated by blowing air in the presence of merox catalyst. The methyl mercaptan is converted to dimethyl disulphide. The reactions involved are:

$$RSH + NaOH \rightarrow RSNa + H_2O$$

$$2\,NaSR + \tfrac{1}{2}\,O_2 + H_2O \rightarrow 2\,NaOH + RSSR$$

The disulphide formed is separated from the caustic in the separator. Merox process unit mainly consist of naphtha merox unit and gasoline merox unit.

The process flow diagram (PFD) of integrated petroleum refining flow sheet is presented in Figure 5.

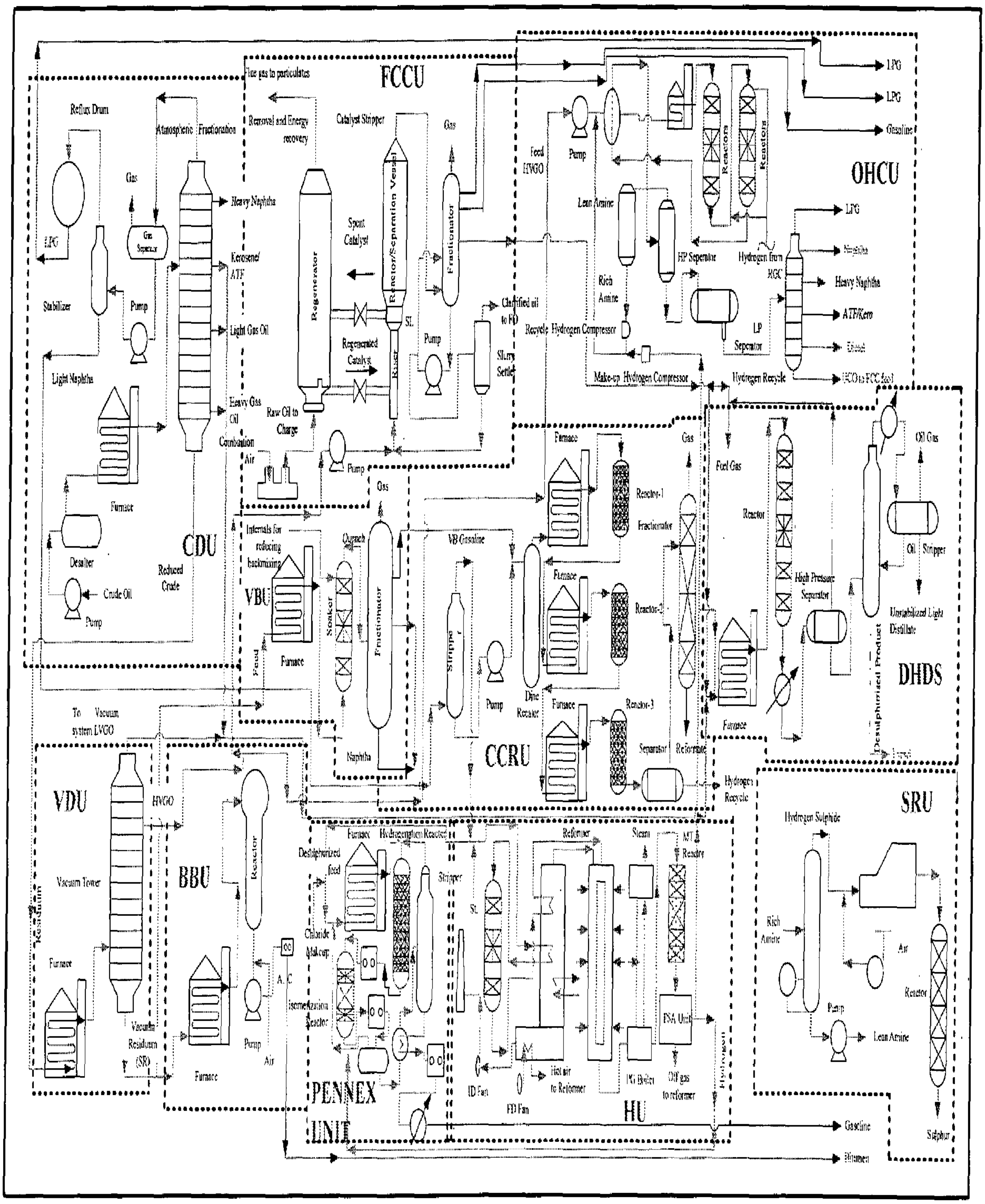


Figure 5: Flow Diagram of an Integrated Petroleum Refinery.

2.3 WASTE STREAMS GENERATED IN PETROLEUM REFINERIES

The petroleum refining industry is a complex and an integrated industry that includes a large variety of processes and products. Because of a large number of processes, use of wide variety of raw materials, catalysts, additives, chemicals, and presence of explosives and hazardous materials; the environmental pollution problem from petroleum refining industries is quite complex. Wide variety of pollutants are discharged into water stream and emitted in the environment. Emission from petroleum complex can be classified into four major categories:

- Storage and handling emissions
- Process emissions
- Fugitive emissions
- Secondary emission

Process emission occurs from reactors, distillation columns, purification equipments, fire heaters, condensers, reformers, crackers, filters, sulphur recovery units, recovery and control equipments, stacks, vents, etc. In almost cases fugitive emission for equipment leaks are the largest source typically accounting for 40 – 60% of total VOCs emission [Siegel, 1997]. Some of the major sources of pollutants in petroleum refinery are crude oil storage, crude processing - desalting and distillation, secondary processes - thermal, catalytic cracking, hydrocracking units, reforming, catalyst regeneration units, hydroprocessing units, lube refining and lube treatment processes, boiler blow downs, power plants, effluent treatment plants, etc. Table 7 summarizes the main pollutant outputs from each refinery process.

Table 7: Typical Material Outputs from Selected Refining Processes

Process	Air Emissions	Process Wastewater	Residual Wastes Generated
Crude oil desalting	Heater stack gas (CO, NO$_x$, SO$_x$, hydrocarbons, and particulates), fugitive emissions (hydrocarbons)	Flow = 2.1 *Gal/Bbl.* Oil, H$_2$S, NH$_3$, phenol, high level of suspended solids, dissolved solids, high BOD, high temperature	Crude oil/desalter sludge (iron rust, clay, sand, water, emulsified oil, wax, and metals)
Atmospheric distillation	Heater stack gas (CO, NO$_x$, SO$_x$, hydrocarbons, and particulates), vent and fugitive emissions (hydrocarbons)	Flow = 26.0 *Gal/Bbl.* Oil, H$_2$S, NH$_3$, suspended solids, chlorides, mercaptans, phenol, elevated pH	Typically, little or residual waste generated
Vacuum distillation	Steam ejector emissions (hydrocarbons), heater stack gas (CO, SO$_x$, NO$_x$, hydrocarbons, and particulates), vent and fugitive emissions (hydrocarbons)	Flow = 26.0 *Gal/Bbl.* Oil, H$_2$S, NH$_3$, suspended solids, chlorides, mercaptans, phenol, elevated pH	Typically, little or residual waste generated
Thermal cracking/ visbreaking	Heater stack gas (CO, SO$_x$, NO$_x$, hydrocarbons, and particulates), vent and fugitive emissions (hydrocarbons)	Flow = 2.0 *Gal/Bbl.* Oil, H$_2$S, NH$_3$, suspended solids, phenol, high pH, BOD$_5$, COD	Typically, little or residual waste generated
Coking	Heater stack gas (CO, SO$_x$, NO$_x$, hydrocarbons, and particulates), vent and fugitive emissions (hydrocarbons) and decoking emissions (hydrocarbons and particulates)	Flow = 1.0 *Gal/Bbl.* High pH, H$_2$S, NH$_3$, suspended solids, COD	Coke dust (carbon particles and hydrocarbons)
Catalytic cracking	Heater stack gas (CO, SO$_x$, NO$_x$, hydrocarbons, and particulates), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO$_x$, SO$_x$, and particulates)	Flow = 15.0 *Gal/Bbl.* High levels of oil, suspended solids, phenol, cyanides, H$_2$S, NH$_3$, high pH, BOD, COD	Spent catalyst (metals from crude oil and hydrocarbons), spent catalyst from electrostatic precipitators (aluminium silicate and metals)
Catalytic hydrocracking	Heater stack gas (CO, SO$_x$, NO$_x$, hydrocarbons, and particulates), fugitive emissions (hydrocarbons) and catalyst regeneration (CO, NO$_x$, SO$_x$, and catalyst dust)	Flow = 2.0 *Gal/Bbl.* High COD, suspended solids, H$_2$S, relatively low levels of BOD	Spent catalyst fines (metals from crude oil and hydrocarbons)

Table 7: Typical Material Outputs from Selected Refining Processes (Contd.)

Hydrotreating/ Hydroprocessing	Heater stack gas (CO, SO_x, NO_x, hydrocarbons, and particulates), vent and fugitive emissions (hydrocarbons), and catalyst regeneration (CO, NO_x, SO_x)	Flow = 1.0 *Gal/Bbl.* H_2S, NH_3, high pH, phenols, suspended solids, BOD, COD	Spent catalyst fines (aluminium silicate and metals)
Alkylation	Heater stack gas (CO, SO_x, NO_x, hydrocarbons, and particulates), vent and fugitive emissions (hydrocarbons)	Low pH, suspended solids, dissolved solids, COD, H_2S, spent sulphuric acid.	Neutralized alkylation sludge (sulphuric acid or calcium chloride hydrocarbons)
Isomerization	Heater stack gas (CO, SO_x, NO_x, hydrocarbons, and particulates), vent and fugitive emissions (hydrocarbons), HCl (potentially in light ends)	Low pH, chloride salts, caustic wash, relatively low H_2S and NH_3	Calcium chloride sludge from neutralized HCl gas.
Polymerization	H_2S from caustic washing	H_2S, NH_3, caustic wash, mercaptans and NH_3, high pH	Spent catalyst containing H_3PO_4
Catalytic reforming	Heater stack gas (CO, SO_x, NO_x, hydrocarbons, and particulates), fugitive emissions (hydrocarbons), and catalyst regeneration (CO, NO_x, SO_x)	Flow = 6.0 *Gal/Bbl.* High level oil, suspended solids, COD, relatively low H_2S	Spent catalyst fines from electrostatic precipitators (alumina silicate and metals)
Solvent extraction	Fugitive solvents	Oil and solvents	Little or no residue wastes generated
Dewaxing	Fugitive solvents, heaters	Oil and solvents	Little or no residue wastes generated
Propane deasphalting	Heater stack gas (CO, SO_x, NO_x, hydrocarbons, and particulates), fugitive propane	Oil and propane	Little or no residue wastes generated
Merox treating	Vents and fugitive emissions (hydrocarbons and disulphides)	Little or no wastewater generated	Spent merox caustic solution, waste oil-disulphide mixture
Wastewater treatment	Fugitive emissions (H_2S, NH_3, and hydrocarbons)	Not applicable	API separator sludge (phenols, metals, and oil), chemical precipitation sludge (chemical coagulants, oil), DAF floats, biological sludges (metals, oils, and suspended solids), spent lime

[**Sources:** Assessment of Atmospheric Emissions from Petroleum Refining, Radian Corp., 1980; Petroleum Refining Hazardous Waste Generation, U.S. EPA, Office of Solid Waste, 1994.]

2.3.1 Air Emissions

Boilers, process heaters, and other process equipments are responsible for the emissions of particulates, carbon monoxide (CO), nitrogen oxides (NO_X), sulphur oxides (SO_X), and carbon dioxide (CO_2). Catalyst changeover and cokers release particulates. Volatile organic compounds (VOCs) such as benzene, toluene, and xylene are released from storage, product loading and handling facilities and oil-water systems; and as fugitive emissions from flanges, valves, seals, and drains. Table 8 represents emission range of these air pollutants per *ton* of crude processed. Major air pollutants that may be emitted from refining operations are sulphur compounds, hydrocarbons, nitrogen oxides, particulates including smoke, and carbon monoxide. Other emissions are aldehydes, ammonia, and odours [Pollution Prevention & Abatement Handbook, 1998].

Table 8: Emission Range of Air Pollutants Emitted per Ton of Crude Processed

Pollutants	**Value (Range)**
Particulate matter	0.8 *Kg* (0.1 – 3.0 *Kg*)
Sulphur oxides (SO_X)	1.3 *Kg* (0.2 – 6.0 *Kg*) 0.1 *Kg* (with Claus Sulphur recovery process)
Nitrogen Oxides (NO_X)	0.3 *Kg* (0.06 – 0.5 *Kg*)
BTX	2.5 *g* (0.75 – 6.0 *g*)
❖ Benzene	0.14 *g*
❖ Xylene	1.8 *g*
❖ Toluene	0.55 g 1 *g* (with Claus Sulphur recovery process)
VOCs	1 *Kg* (0.5 – 6 *Kg*)

[**Source:** Pollution Prevention & Abatement Handbook, 1998]

2.3.2 Wastewater Generation

Petroleum refineries use tremendous amount of water and steam in refinery process ranging from crude oil desalting to FCC units, cokers, hydroprocessing units, and cooling towers. Since water does not enter into the final product, it can be expected that 80 – 90% of water supplied to the refinery comes out as wastewater. Large volume of wastewater is being discharged containing a variety of objectionable and toxic organic and inorganic substances. If this wastewater is not treated to the desired degree, the pollutants reach the water course and bring out a number of changes in the water quality of the receiving water, which ultimately render the water unsafe for aquatic life and for domestic and industrial use. As a general guide, approximately 4 m^3 (3.6 – 5 m^3) of wastewater from processing units are generated per *ton* of crude processed in a typical refinery; and wastewater generated from cooling tower blowdown (CTBD) is additional. Refineries generate polluted wastewater, containing BOD and COD of 150 – 250 *mg/L* and 300 – 600 *mg/L*, respectively; phenol levels of 20 – 200 *mg/L*, oil levels of 100 – 300 *mg/L* in desalter water & upto 5000 *mg/L* in tank bottoms, benzene levels of 1 – 100 *mg/L*, Benzo (a) pyrene levels of less than 1 – 100 *mg/L*, heavy metals of 0.1 – 100 *mg/L* for chrome and 0.2 – 10 *mg/L* for lead, and other pollutants [Pollution Prevention & Abatement Handbook, 1998].

2.3.3 Soil Pollution Hazards

Contamination of soils from the refining process is generally a less significant problem when compared to contamination of air and water. Many residuals are produced during the refining processes and some of them are recycled through other stages in the process. Soil contamination includes some hazardous wastes, spent catalyst or coke dust, tank bottoms, and sludges from the treatment processes can occur from leaks as well as accidents or spill on or off site during the transport process. Refineries generate solid wastes and sludges (ranging from 3 – 5 *Kg/ton* of crude processed), 80% of which may be considered hazardous because of presence of toxic organics and heavy metals [Pollution Prevention & Abatement Handbook, 1998].

The general block diagram of emissions (air, water, and soil) coming from petroleum refineries are given in Figure 6.

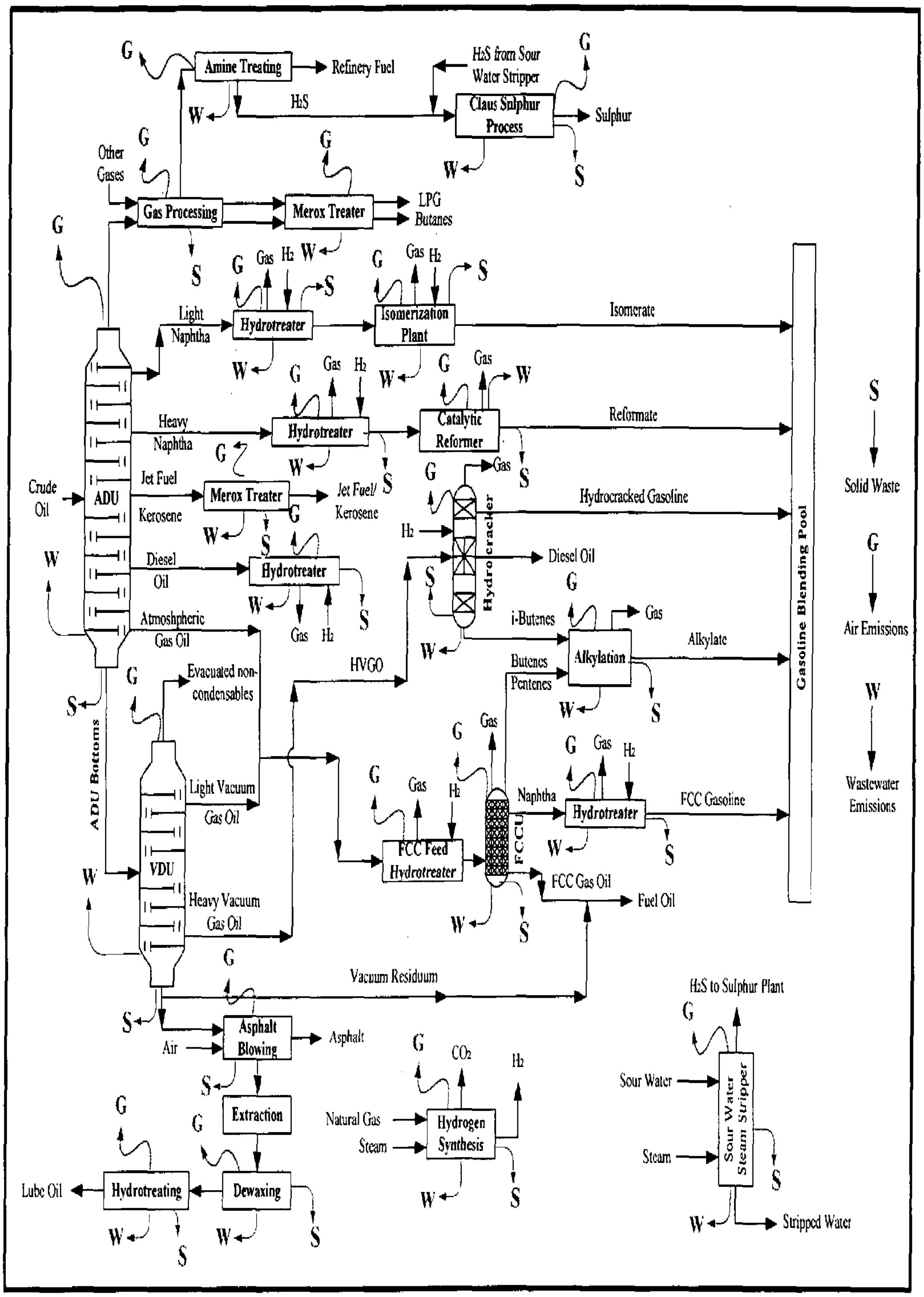


Figure 6: Typical Pollutants Emitted (Air, Water, and Soil) from Petroleum Refineries.

2.4 WASTE MANAGEMENT AND ENVIRONMENTAL POLLUTION CONTROL STRATEGIES

Waste management comprises of quick identification of the waste generated/caused economic reduction, efficient collection and handling, optimal reuse and recycling, effective disposal leaving no environmental problems. Industrial work management has now evolved from an end of pipe treatment mentality to holistic environmental waste management with source reduction as a preferred option [Wang 1998]. The best way to manage waste is not to generate it, however, practically it is not feasible and waste generation is always inevitable. The basic steps for waste reduction are:

- Recognize the waste
- Determine the cause
- Plan corrective action
- Eliminate the cause
- Establish controls to prevent reoccurrence

Due to ever increasing and restrictive environmental regulations, the petroleum refining industries will have to renovate and revamp the waste management facilities by implementing pollutant prevention methods and improved operating and maintenance procedures. The seemingly simple process of removing oil/grease, solids and COD from wastewater is now more challenging due to new requirements for stricter control of hydrocarbon vapours to atmosphere and elimination of the potential for contaminated water into ground and surface water stream [Guida and Fruge, 1995].

Environmental strategic planning begins during conceptual design, construction, startup/operations, and final shutdown facility. Using a life cycle approach which is a cradle-to-grave approach, it will be possible to improve its environmental regulatory compliance and reduce environmental-equipment investment liabilities [Brenneman and Hattaway, 1995].

House keeping procedures, visual inspections, spill prevention program, implementing pollution/waste consciousness training program, supporting plant-wise waste recycling program, conducting leak detection and repair (LDAR) program play key role in minimizing and controlling the generation of wastewater, reducing emissions to air, water and soil.

Wastewater generated from petroleum refining industry is quite complex and contains wide variety of pollutants making the wastewater treatment system more complicated. It is going to be more and more complicated with increasing trend of integration of refinery for value added products. No longer are we only concerned with reducing the level of BOD/COD, but also the specific pollutants. Efficient water management in any large complex is crucial in controlling costs and satisfying environmental obligations. Basic approach for wastewater management is:

- Minimize generation
- Adopt segregation
- In situ reuse/recycle treatment
- Disposal.

Reduction in wastewater generation can be achieved by careful planning and selection of the process method, raw materials, operating conditions, equipments, product substitution, monitoring of water used and wastewater discharge by taking corrective measures. By segregation of wastewater streams, more recycling of water in the process can also help in reduction of waste. To be cost effective multilateral approach that characteristics process streams, identifies contaminant sources, quantifies pollutant level, etc., must be used.

The objective of a effective management plan should concentrate on - review of current and future projects, determination of impacts on wastewater generation, reuse and secondary treatment, development, recommendation to minimize wastewater generation and increase recycle, examination of solids and sludge generation/disposal and recommendation for reduction and treatment options, review of current and future air emissions and proposal for reduction options, determination of effluent quality criteria to meet current and future regulations. Increasingly stringent discharge requirement has necessitated the treatment of the wastewater so that it can be recycled or discharged safely. Water use and wastewater monitoring system is the first step in controlling and regulating the discharge of wastewater. Various wastewater treatment (present and future) technologies are discussed in detail in next chapter.

CHAPTER 3

ENVIRONMENTAL MANAGEMENT PLAN IN PETROLEUM REFINERIES

Rapid industrialization, unplanned urban development, increasing automobile emission has resulted in serious environmental degradation. To defend and to improve environment for present and future generations by making industrial plants healthier and more pleasant to work, mitigating impact of industrialization by eco-friendly greener technologies, preserving ecological balance has become an imperative goal of mankind. The petroleum refining industries are one of the fastest growing Chemical Process Industries (CPI) and are highly polluting ones as they are complex and highly integrated. Petroleum refineries use tremendous amount of water and steam in a variety of processes ranging from crude oil desalting to FCC units, cokers, hydroprocessing units, and cooling towers. Since water does not enter into the final product, it can be expected that 80 – 90% of water supplied to the refinery comes out as wastewater.

3.1 EXISTING WWT TREATMENT AND FUTURE TREATMENT TECHNOLOGIES

Large volumes of water are used by the petroleum refining industries. Four types of wastewater are produced: surface water runoff, cooling water, process water, and sanitary wastewater. Surface water runoff is intermittent and will contains constituents from spills to the surface, leak in equipment, and any materials that may have collected in drains. Runoff surface water also includes water coming from crude and product storage drains. A large portion of water used in petroleum refining is used for cooling. Cooling water typically does not come into direct contact with process oil streams unless and until there is leakage in the exchanger tubes, and therefore, contains less contaminant than process wastewater. Most cooling water is recycled over and over with a bleed or blowdown stream to the wastewater treatment unit to control the concentration of contaminants and the solid contents in the water.

Water used in processing operations also accounts for a significant portion of the total wastewater viz. process wastewater arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains, and boiler blowdown. Because process wastewaters often come into direct contact with oil, it is usually highly contaminated [Sagene, 2003]. Significant pollutants in the refinery wastewater and their potential sources are mentioned in Table 9. Processing and design considerations to reduce pollution from petroleum refineries are presented in Table 10. For effective treatment of the effluent water, the streams are segregated through separate drainage systems and treated accordingly. The water pollution control measures for petroleum refineries can be identified as follows [Chandok et al., 1990]:

(A) Segregation and storage of intermittent spent caustic waste streams arising out of product caustic washes.

(B) Segregation and storage of phenolic condensate streams from cracker, merox, and coker units.

(C) Segregation of sour condensate streams rich in sulphides, ammonia, phenol, and cyanide for in plant stream stripping of sulphides and ammonia.

(D) Segregation of the non-contaminated wastewater like DM plant effluents, boiler blow down, uncontaminated storm run off from off sites and non-process unit areas and once through cooling water if sea water is used for cooling, as if some coastal refineries.

(E) Segregation of oily wastewater from tank bottoms and run off from tank farms, process units for free oil separation and cooling tower blow down (CTBD).

The detailed description of effluent treatment and recycle plant is discussed in the coming section. For effective treatment of the effluent water, the streams are segregated through separate drainage systems and treated accordingly. The general wastewater treatment scheme is presented in Figure 7. Figure 8 gives information about petroleum refinery effluent and possible choices for wastewater treatment and their sequences.

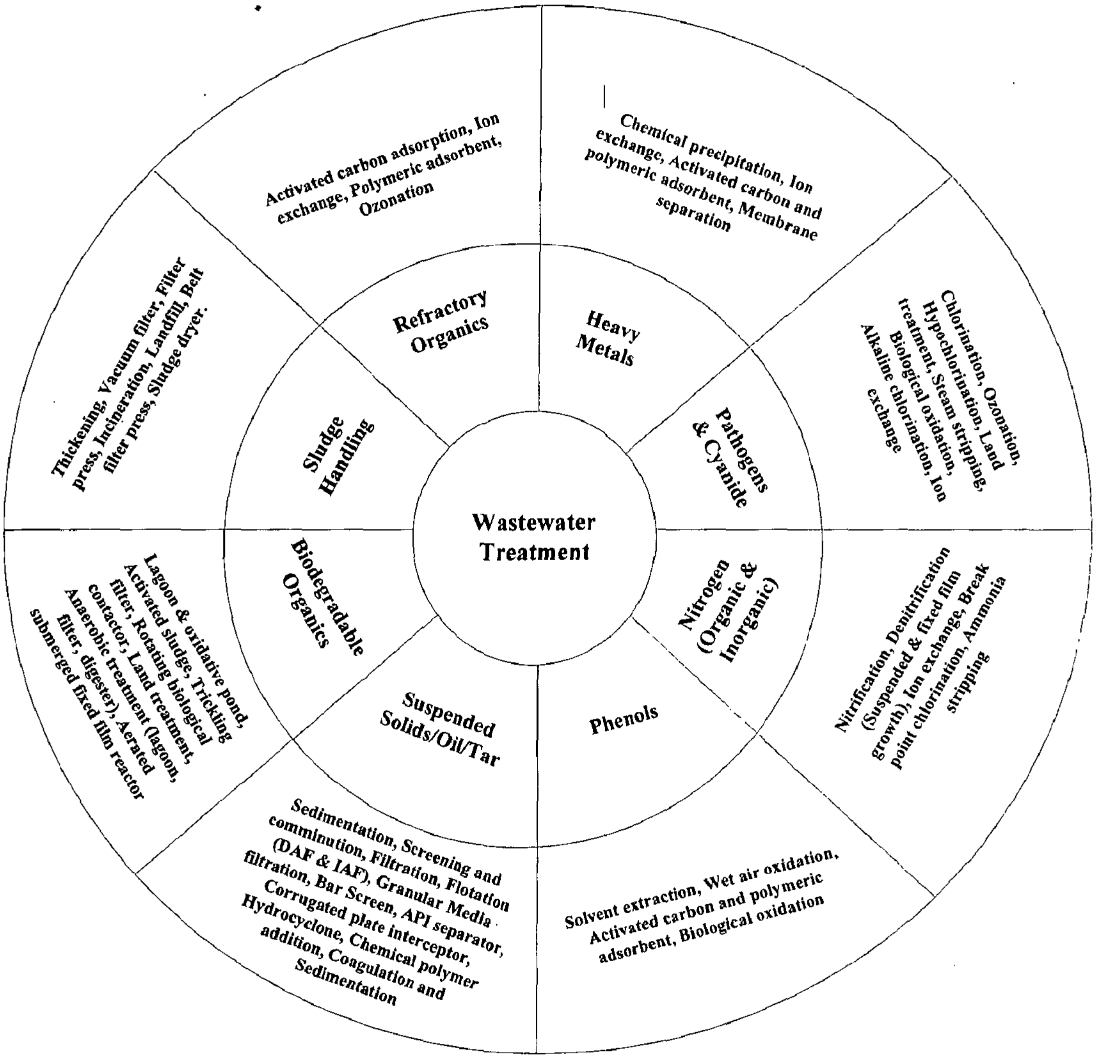


Figure 7: General Wastewater Treatment Scheme.

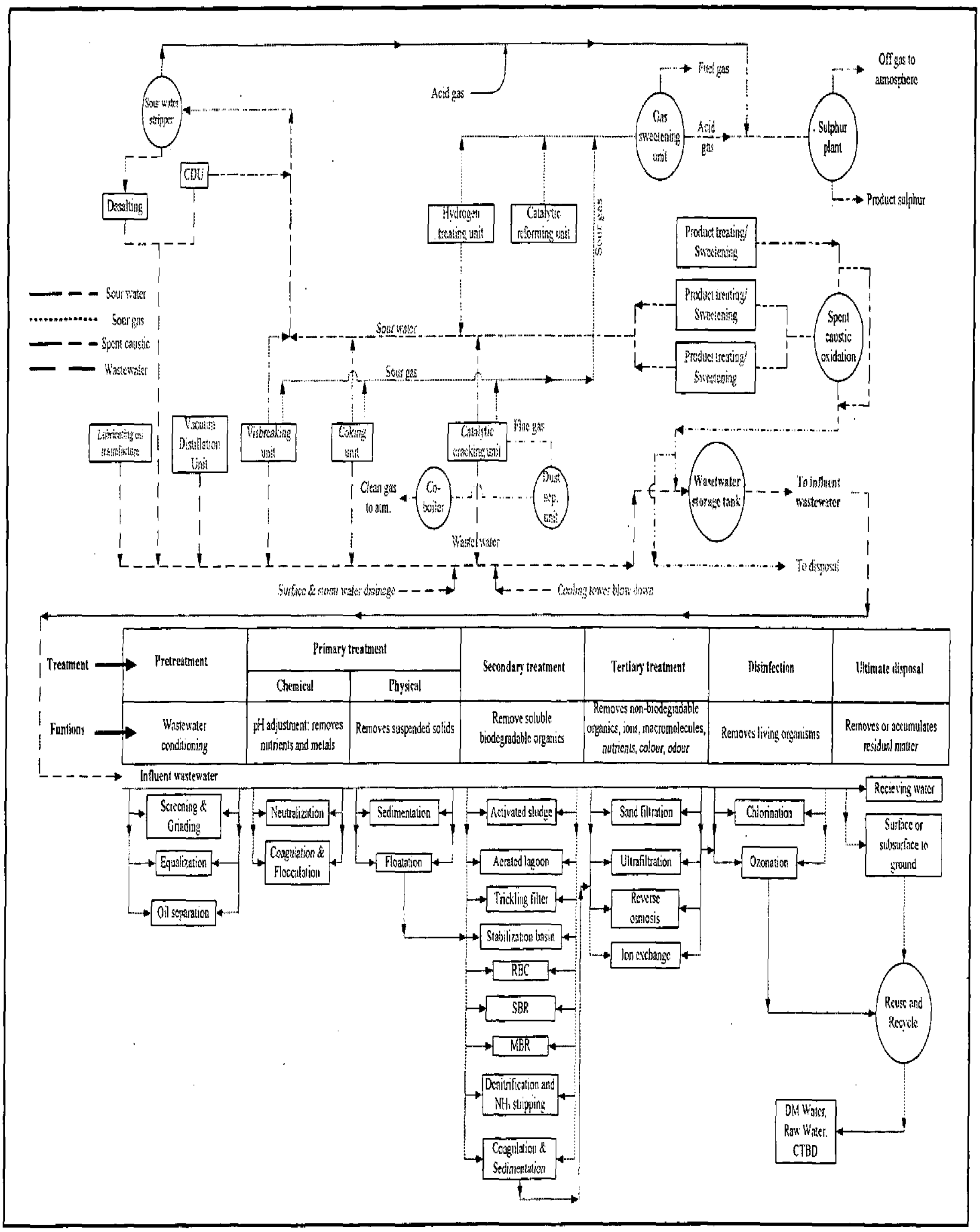


Figure 8: Flow Diagram of Petroleum Refinery Effluent & Possible Choices for Wastewater Treatment and Their Sequences.

Table 9: Significant Pollutants in Refinery Wastewater & Emissions and Their Potential Sources

S. No.	Pollutant Parameter	Origin of Pollutant	Waste Streams contributing the Pollutants
Pollutants in Refinery Wastewater			
1.	BOD	Soluble hydrocarbons and sulphides	Crude fractionation, thermal/catalytic cracking and solvent refining processes, leaks and spills from product storage and finishing operations
2.	COD	Oxidizable organics	Cracking air lube oil processing, leaks and spills from crude and product storage, loading and unloading areas
3.	Oil and grease	Crude, intermediate or finished products	Spills, wash down, vessel cleanouts and sampling point overflow
4.	Ammonia		Overhead condensates from crude fractionation, cracking, and from desalting operations
5.	Phenolic compounds	Product of side reactions during refinery operations	Thermal and catalytic cracking product finishing and treating
6.	Sulphides	Sulphur in the crude	Crude desalting, distillation, and cracking product treating process
7.	Suspended solids (SS)	Inorganic components are sand, silt, clay and organic fraction includes oil, tar, fibers	Crude desalting, distillation, cracking and finishing operations
8.	pH	Acidity is because of mineral acids viz. H_2SO_4, HF, H_3PO_4, etc., and week organic acids viz. carboxyl and carbonic acid. NH_3 and NaOH used contribute to alkalinity.	Alkylation and polymerization processes result in severe acidity problem. Product treating viz. sweetening processes, crude distillation, cracking processes results in alkaline waste streams
9.	Cyanides	Product of side reaction	Catalytic cracking process
10.	Chromium	Generally present as chromate; used as corrosion inhibitor in cooling water	Cooling tower blow down
11.	Oxides of sulphur (SO_X)	Sulphur in the crude	Process heaters, boilers, product treating units, catalytic cracking unit, regenerator flare and decoking operations
12.	Oxides of nitrogen (NO_X)	Product of combustion reactions	Process heaters, boilers, catalyst regenerators, flares
13.	Hydrocarbons	Intermediates and product hydrocarbons	Loading facilities, storage tanks, catalyst regenerator, vacuum jets, barometric condensers, blow down system, leaks from valves/pumps and compressors, process heaters, boilers
14.	Particulate matter	Coke particles catalyst fines	Decoking operations, catalyst regenerators, boilers, process heaters, incinerators
15.	Carbon monoxide (CO)		Catalyst regenerator, decoking operations and incinerator
16.	Aldehydes and ammonia		Catalyst regenerators

Table 10: Process and Engineering Design Considerations to Reduce Pollution from Petroleum refineries

Design Criteria	Measures
Process Design Considerations	
(A) Process selection	➢ Considerations for type of effluent and emissions when comparing alternative processes. ➢ Substitution of continuous processes for batch treatment wherever possible. ➢ Management of spent caustic. ➢ Floating roof, pressure tanks for storage. ➢ Oil-water system must be closed during treatment. ➢ Use of surface condensers instead of barometric condensers wherever possible.
(B) Product and chemical losses	➢ Installation of measures to restrict carryovers. ➢ Suitable chemical recovery processes in solvent refining and dewaxing processes, etc.
(C) Modified operating conditions	➢ Reuse and recycle of water viz. use of stripped water in crude desalter, recycle of water from coking operations, etc., and treatment of VOCs should be done with care. ➢ Reuse of condensate (steam) as boiler feed water. ➢ Use of closed loop for compressor and pump cooling water. ➢ Use of air cooling wherever feasible.
Engineering Design Considerations	
(A) Separate drainage and sewer systems	➢ Separate collection system for clean wastewater viz. cooling tower blowdown, unpolluted storm water, oily/polluted water, sanitary sewage
(B) Segregation of wastewater streams	➢ Segregation of process waste streams depending upon the type of composition viz. spent caustic, raw sour water, etc., for suitable in-plant treatment to outside-battery limit.
(C) Systems for blowdown and turn around	➢ Smokeless flares, suitable vapour recovery system. ➢ Depressurizing and purging to vapour recovery system prior to opening of vessels during turn around

3.2 PRIMARY TREATMENT METHODS

Primary wastewater treatment consists of the separation of oil, water, and solids in two stages. During the first stage, an API separator, a corrugated plate interceptor, or other separator design is used.

3.2.1 API Separator

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. API separators are normally designed to remove oil to the extent of 50 – 100 *ppm* in water. The gravity separators are essentially rectangular chambers equipped with oil skimming and sludge scrapping devices and design of the separators is based on the removal of oil globules of 0.015 *cm* (150 μm) in diameter and above.

Wastewater moves very slowly through the separator allowing free oil to float to the surface and be skimmed off, and solids to settle to the bottom and be scraped off to a sludge collecting hopper. These separators are normally operated without using any chemicals or coagulants or aids. Oil and grease separated from these units as slop oil are recovered and reused in the refinery. Modern API separator is closed from the top with VOCs removal and treatment facilities and automatic oil skimming devices.

3.2.2 Tilted Plate Interceptor (TPI)/Corrugated Plate Interceptor (CPI)

Traditionally oil – water separation in effluents from petroleum refineries has been achieved by means of API separator as the first separation step but it has certain disadvantages and they are: construction cost, space requirements, evaporation losses, fire hazards, high steam-consumption to avoid freezing of heavier products. Moreover, it can not remove oil globule below 150 μm size. API separator is a rugged unit and can sustain fluctuation in flow and oil load. However, API can not remove higher oil load or oil containing high wax content. So TPI unit is put after API system for the efficient removal of free oil.

In a TPI, the oil path has been reduced to a slight distance by a set of parallel plates inclined at 45^{O}. Oil coagulates at the undersurface of each plate and slides upward to the liquid surface where it can be skimmed off. Furthermore, solid particles collect on the top of each plate and slide down to the bottom. These properties make a

TPI much smaller than its equivalent API separator, which allows automatic oil recovery without skimmers.

The second stage utilizes physical or chemical methods to separate emulsified oils from the wastewater. Physical methods may include the use of a series of settling ponds with a long retention time which are obsolete; and are not in practice now days, however, the use of DAF/DGF/IAI/CAF provides better and efficient means to remove emulsified oil. Chemical methods include the use of chemical coagulation and clarification.

3.2.3 Chemical Coagulation and Clarification

The main purpose of chemical method is to remove emulsified oil with the addition of flocculating agents and also to remove suspended solids and toxic substances and thereby condition the effluents for further treatment by biological method. These chemical methods are used when emulsified oil present in wastewater is significantly high which cannot be removed by gravity oil separator. Various chemical methods available can be further classified under the following four categories:

(a) Neutralization
(b) Precipitation and clarification method
(c) Chemical oxidation method
(d) Regeneration method

The above objective can be achieved by adjusting the pH of the wastewater between 5 and 6 and subsequently precipitating the sulphonic and napthenic acids as water insoluble calcium salts by the addition of hydrated lime until a pH of 7.7 – 8.5 is reached. Various coagulating agents like ferrous sulphate, ferric sulphate (chlorinated copperas), calcium chloride, calcium carbonate and hydrated lime, have been used to de-emulsify an oil separator effluent. The flocs that are formed by such treatment adsorb most of the oil, and depending on the initial oil concentration, an effluent may be produced with an oil content of 10 *mg/L*, or even less. The above method discussed below is about coagulation and flocculation which is generally done in a refinery. However, a cost effective chemical dosing system is observed to be ferrous sulphate (100 *mg/L*), lime (50 *mg/L*) and fuller's earth (5 *mg/L*) to bring down the sulphides from 300 *mg/L* to 20 – 30 *mg/L*, emulsified oil to less than 20 – 30 *mg/L* and cyanides from 10 – 12 *mg/L* to 2 – 3 *mg/L* as CN^-.

3.2.4 Dissolved Air Flotation (DAF)

Dissolved air flotation (DAF) consists of saturating a portion of the wastewater feed, or a portion of the feed or recycled effluent from the flotation unit with air at a pressure of 40 – 60 *psig*. The wastewater or effluent recycle is held at this pressure for 1 – 2 *min* in a retention tank and then released at atmospheric pressure to the flotation chamber. The sudden reduction in pressure results in the release of microscopic air bubbles which attach themselves to oil and suspended particles in the wastewater in the flotation chamber.

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 chamber is usually 10 – 20 *min*. The effectiveness of DAF depends upon the attachment of bubbles to the suspended oil and other particles which are to be removed from the waste stream. Chemical flocculating agents, such as salts of iron and aluminium, with or without organic polyelectrolytes, are also helpful in improving the effectiveness of the DAF process.

3.2.5 Cavitation Air Flotation (CAF)

A CAF system is a flotation system and is an alternate to DAF system for the removal of oil, grease, colloidal, and suspended solids. The CAF system possesses certain advantages over DAF system, as DAF systems are often complex, expensive, and can also suffer operational problems such as blockages occur in nozzle through which water is ejected. These problems are not encountered with CAF system. By operation of cavitation aerator, micro-bubbles can be injected directly into the effluent without the need to dissolve the air first. This means that only air passes through the ejection mode and, therefore, no blocking can occur. The recirculation rate provided in CAF system is much greater than DAF system and continuous recirculation is provided from various points on the bottom of flotation tank which reduces the possibility of solid deposition. Most important of all, the effluent and the recirculation water don't pass through any nozzles/orifices, thus blocking simply cannot occur. Since no compressors, pumps are required, it is however, an extremely efficient solid removal system, with very low maintenance and operating costs.

After the removal of suspended solids in DAF/CAF system, the next step generally involves the removal of various contaminants including sulphides, mercaptans and phenols (cresylates), as well as emulsified hydrocarbons before sending it to the biological treatment system as it ruptures entire biological system. Oxidizing chemicals like chlorine and ozone are employed for removal as phenol is oxidized to carbon dioxide and water, and cyanide is oxidized to carbon dioxide and nitrogen. Direct combustion is applied to burning of certain sulphide/phenolic wastes, where the flow is lean and COD of waste is high. Production of spent caustic solutions is reduced by the regeneration of chemicals like monoethanolamine which is used to absorb hydrogen sulphide and mercaptans. It is regenerated by steam stripping for further use. The hydrogen sulphide gas thus liberated is subjected to sulphur removal in a sulphur recovery unit (SRU).

3.2.6 Flow Equalization

The purpose of equalization is to mitigate surges in flows and pollutant loadings. This is necessary for biological treatment plant, as high concentration of certain materials will upset or completely kill the bacteria in the treatment plant. The equalization step traditionally consists of a large pond, which are now being replaced by closed tanks due to the enforcement of new VOCs norms. The equalization step should be after free oil removal in a gravity separator.

3.3 SECONDARY TREATMENT METHODS

The biological treatment aims at the removal of all oxidizable and organic matter from the wastewater. In this treatment processes, dissolved oil and other organic pollutants may be consumed biologically by micro-organisms. Biological treatment may require the addition of oxygen through a number of different techniques, including activated sludge units, trickling filters, oxidation ponds, aerated lagoons, and rotating biological contactors. Secondary treatment generates bio-mass waste which is typically treated anaerobically, and then dewatered.

3.3.1 Oxidation Ponds

The treatment of wastewater in oxidation ponds provides biological oxidation and sedimentation similar to that occurring in lakes. Its main attraction is the low cost of construction and operation, but it requires more space and considerably long detention periods (11 – 110 *days*). An oxidation pond has a large surface area and has a shallow depth, usually not exceeding 2 *m*. The shallow depth allows the oxidation pond to be operated aerobically without mechanical aerators. The algae in the pond produce oxygen by means of photosynthesis. This is then used by bacteria to oxidize the wastewater. Because of low loadings, little biological sludge is produced, and the pond is fairly resistant to upsets due to shock loadings. This process is no more applicable in the treatment of refinery waste.

3.3.2 Aerated Lagoons

The aerated lagoon is a smaller, deeper oxidation pond equipped with mechanical aerators or diffused air units. The addition of oxygen enables the aerated lagoon to have a higher concentration of microbes than the oxidation pond. The retention time in aerated lagoons is usually shorter, between 3 – 10 *days*. More aerated lagoons are operated without final clarification. As a result, biomass is discharged in the effluent, causing the effluent to have high BOD and solids concentration. Where effluent standards are stringent, final clarification is necessary. This process is no more applicable in the treatment of refinery waste.

3.3.3 Trickling Filters

The trickling filter is a packed media covered with biological slime through which wastewater is percolated. The slime layer consists of one aerobic and one anaerobic sub layer. In the biological aerobic process, which takes place in the aerobic sub layer, the substrate is partially oxidized to provide energy for the biological process. Another part of substrate is utilized to synthesize new slime material. In the anaerobic sub layer, decomposition takes place with formation of organic acids, CH_4, and H_2S. In the trickling filter, organic colloidal particles are removed by aerobic oxidation, biosorption, coagulation, and aerobic decomposition. Usually, the thickness of slime layer is between 0.1 and 2.0 *mm*. It has adverse effect of operation of trickling filter if it is thicker than 2.0 *mm*. Some of the advantages of trickling filter over activated sludge process are that it requires no power requirements for aeration; it is simple to operate, and quicker recovery to sudden changes of influent BOD.

3.3.4 Rotating Biological Contactors (RBC)

Rotating Biological Contactors (RBC), analogues to trickling filters, are fixed-film reactors. Bacterial slime grows on plastic discs rotating through the wastewater. Approximately, half of the circular disc is out of the water at any one time, being aerated, and half is under water supporting biological growth. The discs rotate slowly, requiring minimal power. Discharge from an RBC may need clarification to remove suspended material generated in the fixed growth process.

3.3.5 Activated Sludge Process (ASP)

Activated sludge is an aerobic treatment process in which high concentrations (1500 – 3000 *mg/L*) of newly grown and recycled micro-organisms are suspended uniformly throughout a holding tank to which raw wastewater are added. Oxygen is introduced by mechanical aerators, diffused air systems, or by other means. The organic materials in the waste are removed from the aqueous phase by the microbiological growths and stabilized by biochemical synthesis and oxidation reactions.

It consists of an aeration tank followed by sedimentation clarifier tank. The flocculent microbial growth removed in the sedimentation tank is recycled to the aeration tank to maintain a high concentration of active micro-organisms. Although the micro-organisms remove almost all of the organic matter from the waste being treated, much of the converted organic matter remains in the system is in the form of microbial cells. These cells have relatively high rate of oxygen demand and must be removed from the treated wastewater before discharge. Thus, final sedimentation and recirculation of biological solids are important elements in an activated sludge systems.

3.3.6 Sequencing Batch Reactors (SBR)

The sequencing batch reactors (SBR) process utilizes a fill-and-draw reactor with complete mixing during the batch reaction step (after filling) and where the subsequent steps of aeration and clarification occur in the same tank. All SBR have five steps in common, which are carried out in sequence as follows:

(1) **Fill:** During the fill operation, volume and substrate are added to the reactor. The fill process typically allows the liquid level in reactor to rise from 75 – 100% of the capacity. When two reactors are used, the fill

process may last 50% of cycle time. The reactor may be mixed only or mixed and aerated to promote biological reactions.

(2) **React:** During the react period, the biomass consumes the substrate under environmental conditions.

(3) **Settle:** Solids are allowed to separate from the liquid under quiescent conditions, resulting in a clarified supernatant that can be discharged as effluent.

(4) **Decant:** Clarified effluent is removed during decant period.

(5) **Idle:** An idle period is used in a multitank system to provide time for one reactor to complete its fill phase before switching to another unit.

3.3.7 Membrane Bio Reactor (MBR)

Membrane biological reactors (MBRs), consisting of a biological reactor (bioreactor) with suspended biomass and solids separation by microfiltration membranes with nominal pore sizes ranging from 0.1 – 0.4 μm, are finding wide applications in wastewater treatment and is one of the latest treatment technologies in biological treatment. Submerged membranes are used in place of clarifiers to separate sludge from wastewater so as to produce high quality permeate. The concept of MBR systems consists of utilizing a bioreactor and microfiltration as one unit process for wastewater treatment thereby replacing solids separation function of secondary clarification and effluent filtration. These MBRs can handle very high sludge concentrations in the aeration tank because of which the size of aeration tank reduces four to five folds. As the membrane acts as fine filter, it does not require any further treatment using sand filters, activated carbon filters, etc.

3.4 TERTIARY TREATMENT METHODS

Some refineries employ an additional stage of wastewater treatment called polishing (activated carbon filtration process) or ozonation to meet discharge limits and which are effective in removal of the taste, odour, and organics from biologically treated wastewaters. The polishing step can involve the use of activated carbon, anthracite coal, or sand to filter out any remaining impurities, such as biomass, silt, trace metals, and other inorganic chemicals, as well as any remaining organic chemicals. The treated water which satisfies the relevant tolerance limits are finally disposed by controlled dilution into the neighbouring streams, river or sea or it is recycled/reused in the complex itself.

3.4.1 Activated Carbon (AC)

Activated carbon is potentially a very promising and flexible method of tertiary treatment. The activated carbon (AC) process utilizes granular activated carbon to adsorb pollutants from wastewater. An AC unit comprises of sand filter which prevents plugging of carbon pores. From the filter, water flows to a bank of carbon columns arranged in series or parallel. As the water flows through the columns, the pollutants are adsorbed by the carbon, gradually filling the pores. At intervals, portions of the carbon are removed to a furnace where the adsorbed substances are burnt off. The regenerated carbon is reused in the columns, with some make up added, because of handling and efficiency losses. Its use is increased because AC can remove not only organic materials along with biological treatment. This method removes 95% of the dissolved organics from a typically refinery wastewater.

3.4.2 Chlorination

Chlorination is probably the most commonly used process today for final chemical treatment of wastewater. Chlorine compounds used include calcium hypochlorite, sodium hypochlorite, and pure chlorine. The clear overflow from clarifier flows to a chlorine contact tank (CCT). Chlorine is bubbled in the mixing chamber of chlorine caustic tank for disinfection and chemical oxidation of organics. The partially treated effluent overflows to the filter feed sump. At the end of chlorination tank, the residual chlorine in water is maintained below 0.2 *ppm*.

3.4.3 Ion Exchange

Ion exchange as a tertiary technique is used for the removal of ions present in the water. It is employed where high degree of ion removal is required. Generally, ion exchange is used in the demineralization of boiler water feeds. It is applied after reverse osmosis (RO) in tertiary treatment plant system, where further removal of ions is envisaged.

3.5 MEMBRANE PROCESSES

Membrane processes refers to the treatment processes that are non-biological in nature. Membrane processes used can be categorized into four classes according to the size of particles that can be retained, viz. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO). RO is also extensively used in desalting operations. It has an added advantage of being able to remove many organic compounds in addition to ionic species and micro-organisms. The NF, MF, UF techniques are useful in removing macromolecules, colloids, and suspended solids. These membrane processes are chosen according to the size range of solutes in the solution. These processes require less land than that of biological processes and less amount of sludge is produced. A general overview of membrane separation technology is presented in Figure 9 [Vigneswaran and Viswanathan, 2000].

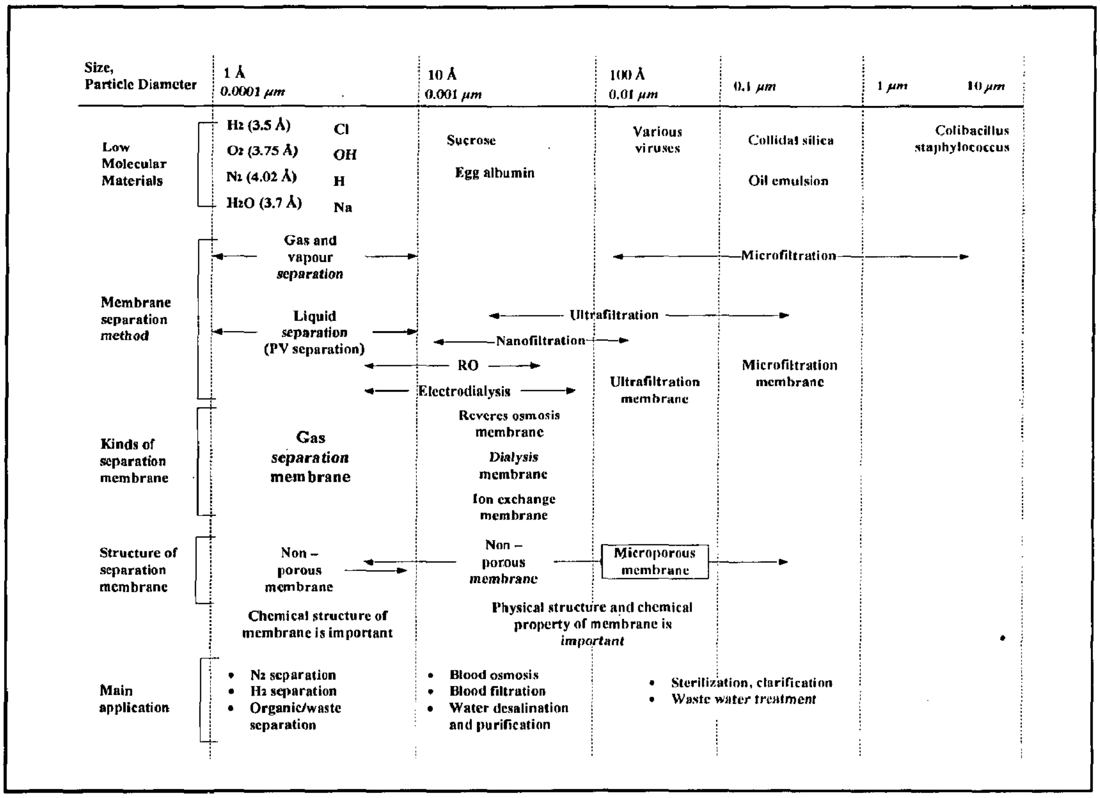


Figure 9: Overview of Membrane Separation Technology.

3.5.1 Microfiltration

Microfiltration is an important separation process, as the permeate flux is higher than that of any other membrane processes and the permeate quality is much more better than that of the conventional separation processes such as sedimentation, centrifugation, filtration, flotation, etc. Most of the pollutants produced in the water have particle sizes ranging from 0.05 – 10 *μm* and can be removed by MF as they fall within the range of microfiltration process. MF membranes can retain species much smaller than their rated pore size due to adsorptive capture. MF membranes typically operate at 0.5 – 5 *bars* pressure.

3.5.2 Ultrafiltration

Ultrafiltration (UF) membranes allow the passage of water and retain high molecular weight solutes and colloidal particles. UF pore sizes usually ranges from 5 – 20 *nm* and retain fine colloids, macromolecules, and micro-organisms. Partial retention of some ions may occur due to the charge interaction. UF membranes typically operate with the pressures in the range of 1 – 4 *bars*. UF is widely used to produce sterilized water and the major advantages of UF are that it operates at lower pressure and yields a higher permeate reflux compared to RO.

3.5.3 Nanofiltration

The nanofiltration membranes (NF) are believed to have pores (2 – 5 *nm*) and partially retain ions, through small and mono-valent ions, and low molecular weight organics tend to pass. NF membranes usually have significantly higher water permeability than that of RO membranes and also operate at lower pressure (typically 7 – 30 *bars*). NF membranes should be capable of removing most contaminants including aluminium in its various forms. Normally it is used for the softening of water in water applications.

3.5.4 Reverse Osmosis

Reverse osmosis (RO) is based on the well known phenomenon of osmosis, which occurs when two solutions of different concentrations are separated by means of a semi-permeable membrane. In this process, pressure is applied on the side of the concentrated solution to reverse the natural osmotic flow. The thin RO membranes are essentially non-porous and they preferentially pass water and retain most solutes including ions. The rejection of ions is typically in the range 95 – 99% depending on the ions and the membrane. RO is characterized by operating pressure (20 – 100 *bars*). Possible uses in the refinery are treatment of cooling tower blowdown, boiler water blowdown, WWTP rinses, API separator effluent, etc.

Table 11 summarizes the main treatment technologies their advantages, disadvantages, operation control, and compliance parameters. The general block diagram of a general existing effluent treatment plant and hybrid integrated effluent treatment system in a refinery are presented in Figure 10 and 11, respectively.

Table 11: Main Treatment Technologies: Advantages and Disadvantages, Operation Control and Compliance Parameters

Treatment method	Advantages	Typical risks and problems	Operation control parameters	Compliance parameters
Screening	➢ Removes large suspended solids and consequently ➢ Partially reduces pollution load ➢ Flow homogenization	➢ Blockage, overflows or odour problems could arise due to infrequent cleaning	➢ Influent TSS level ➢ Fouling ➢ Pressure drop ➢ Flow rate	➢ TSS
API & CPI separators	➢ Simple design ➢ Handles larger capacity ➢ Minimum mechanical and electrical requirements ➢ Low operation and maintenance costs	➢ Large area requirement ➢ Limited to removal of free oil and grease	➢ Influent oil and grease ➢ Flow rate	➢ Free oil and grease
Flow equalization	➢ Reduce size and cost of downstream treatment facilities	➢ Requires large area in case of high flow rate ➢ Anaerobic condition if not aerated	➢ Retention time	➢ Turbidity
Settling basins	➢ Easy to operate ➢ Steadiness of treatment operations (reduced shock loads)	➢ Improper control over sedimentation tanks may cause solids and BOD overloading problems ➢ Fouling ➢ Large area requirement	➢ Retention time ➢ Inlet flow	➢ TSS
Lamella separators	➢ Higher separation efficiency ➢ Easy discharge of settled sludge ➢ Less area required	➢ Cleaning problems	➢ Influent TSS level ➢ Flow rate ➢ Fouling	➢ TSS
Coalescence	➢ Small and compact ➢ Easy operation and maintenance ➢ Low cost	➢ Limited capacity ➢ Partial removal of emulsified oil		
DAF system	➢ Removal of both free and emulsified oil ➢ Removal of both floating and settleable solids ➢ Very small and light particles can be removed completely in short time	➢ High chemical consumption ➢ Relatively high sludge formation	➢ Influent oil and grease concentration level ➢ Influent TSS level ➢ Chemical doses ➢ Input flow rate ➢ Air pressure	➢ TSS ➢ Total oil and grease ➢ COD

Table 11: Main Treatment Technologies: Advantages and Disadvantages, Operation Control and Compliance Parameters (Contd.)

Conventional activated sludge	➢ Low land required ➢ No problem of flies	➢ High energy consumption ➢ Sludge bulking ➢ Requires very highly skilled professional to operate	➢ MLSS ➢ MLVSS ➢ DO levels ➢ Nutrient doses ➢ Air flow ➢ Settleability	➢ BOD ➢ COD
Extended aeration systems	➢ Sludge is partially digested within air tank ➢ More resistance to incoming shock load	➢ Retention time in final clarifier is twice than that of conventional system ➢ High oxygen consumption of oxygen	➢ MLSS ➢ MLVSS ➢ DO levels ➢ Settleability	➢ BOD ➢ COD
Aerated ponds	➢ Good BOD removal	➢ Higher sludge production ➢ High suspended solids in the effluent	➢ DO levels	➢ BOD
Trickling filters	➢ Low equipment and power costs ➢ Shock loading can be absorbed ➢ Minimum sludge produced	➢ Fly and odour nuisance ➢ Limited capacity ➢ Pounding and clogging of filters	➢ Nutrient doses ➢ DO levels ➢ Air flow	➢ BOD ➢ COD
Bio tower	➢ Minimum sludge formation ➢ Vertical design, less area required	➢ Fly and odour nuisance ➢ Limited capacity ➢ Pounding and clogging of filters	➢ DO levels ➢ Nutrient doses ➢ Retention time ➢ Air flow ➢ MLSS ➢ MLVSS	➢ BOD ➢ COD
Anaerobic treatment	➢ High organic pollution load ➢ Less sludge production	➢ Biogas production ➢ Temperature required (30^0C) ➢ Very sensitive to shock load	➢ Methane production ➢ H_2S level	➢ BOD ➢ COD
SBR	➢ Higher efficiency ➢ Save on area as no separate clarifier is required ➢ Less sludge formation	➢ High power consumption ➢ Failure if any problem occurs in the automatic control system	➢ Retention time ➢ Air flow ➢ Air bubbles distribution ➢ DO levels	➢ COD ➢ TSS ➢ BOD

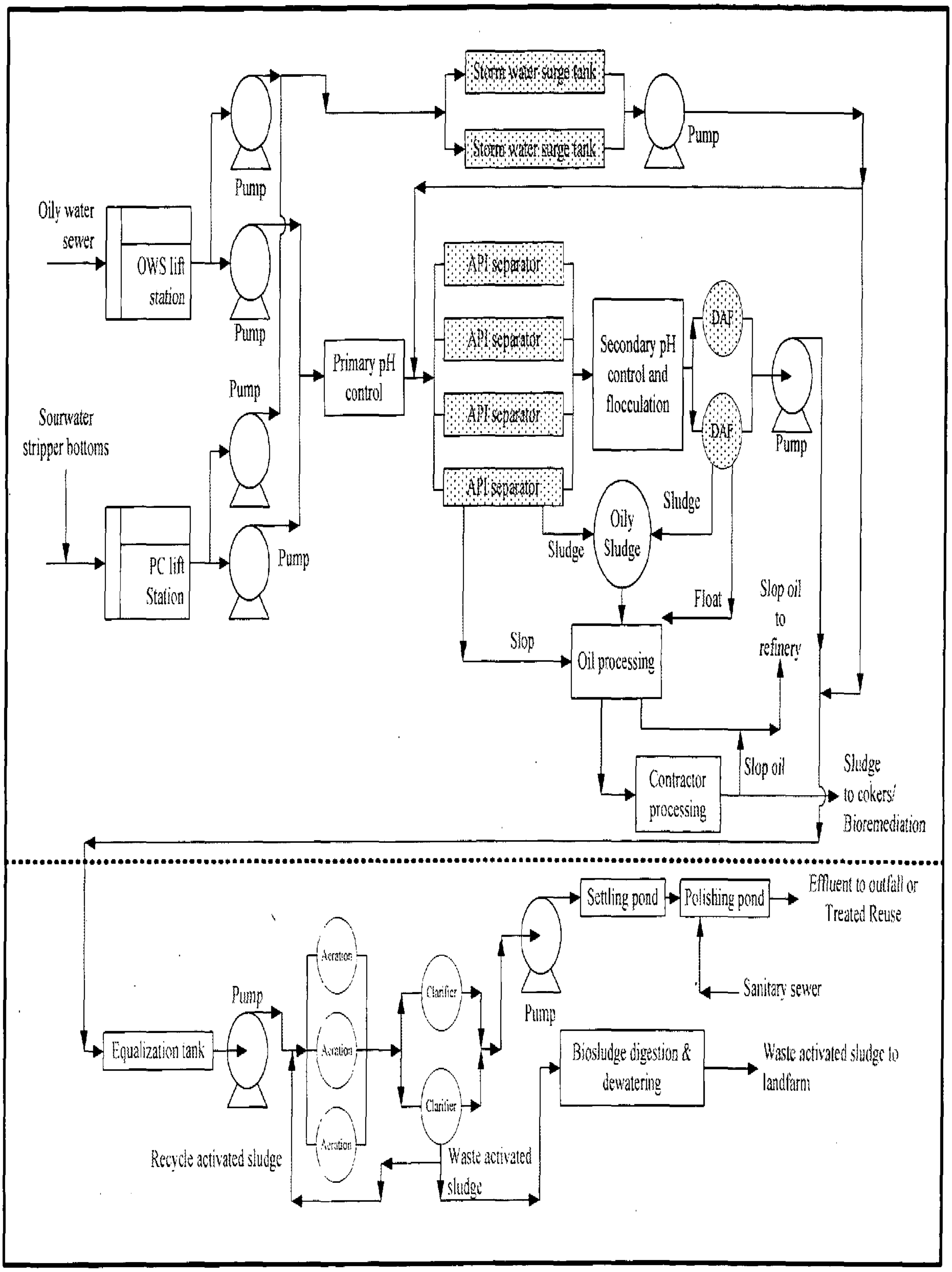


Figure 10: Existing Wastewater Treatment Plant in Petroleum Refineries.

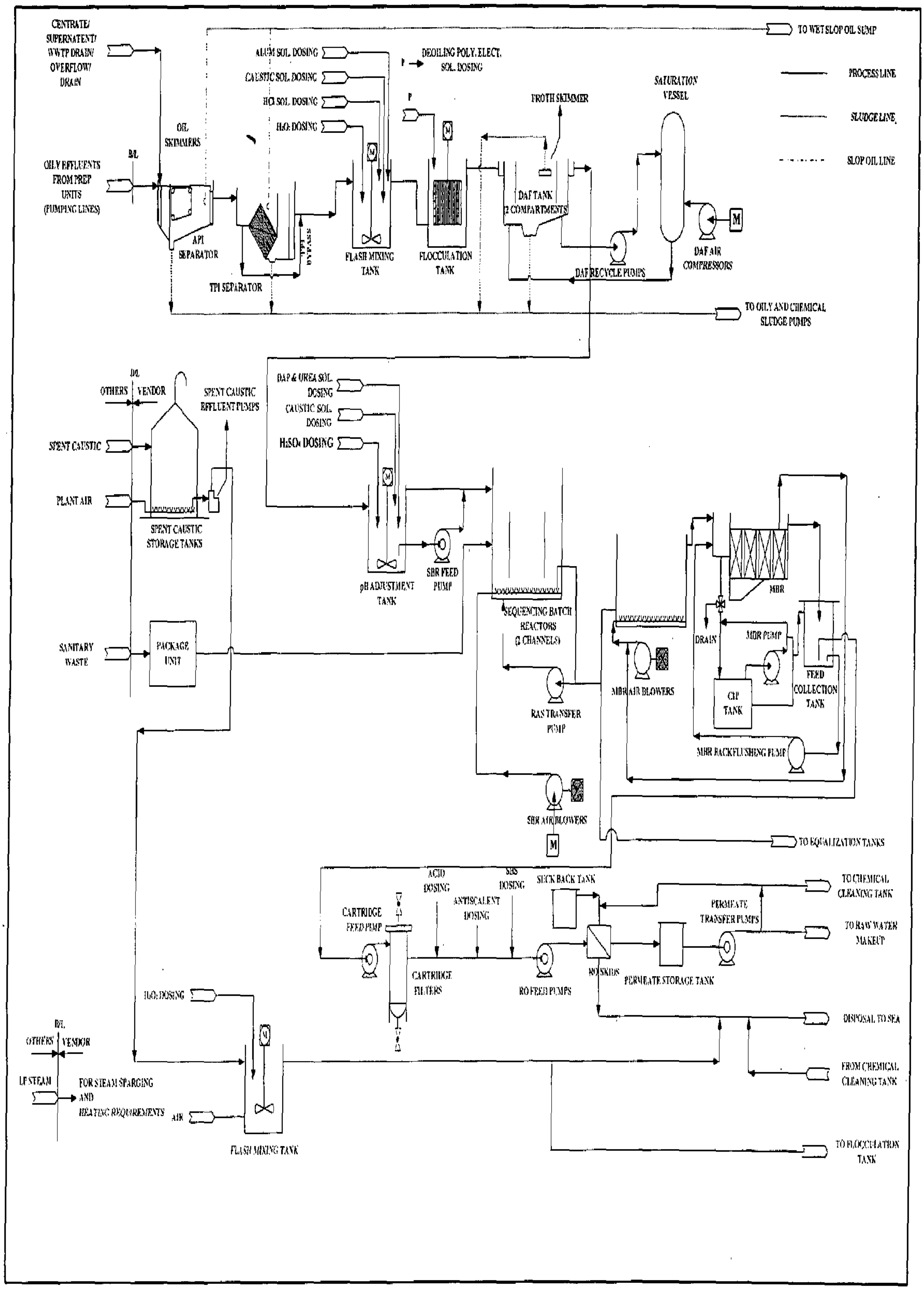


Figure 11: Process Flow Diagram of Proposed Hybrid Integrated Effluent Treatment System.

CHAPTER 4

LITERATURE REVIEW

4.1 LITERATURE REVIEW

Petroleum refineries separate crude oil into a wide array of petroleum products through a series of physical and chemical separation techniques. These techniques include fractionation, cracking, hydrotreating, combination/blending processes, and manufacturing and transport. Petroleum refining is one of the largest industries in India and a vital part of national economy. Waste disposal in the oil fields and refineries contributes to environmental pollution. Refinery wastes contain oily water, chemicals, ballast, sanitary wastes, toxic liquids, gases and vapours in various combinations which pollute the soil and the atmosphere. However, potential environmental hazards associated with refineries have caused increased concern for communities in close proximity to them. This update will provide us information that a lot of work was done in the field of mitigation of pollutants concentration in the waste streams and various changes in the design are to be incorporated in the entire complex process of the integrated refinery. Steps to reduce or eliminate environmental pollution due to refinery wastes are briefly discussed in this chapter. Some of the papers have been discussed here under:

Huang (1971) had attempted to treat a refinery waste by physicochemical processes to evaluate the feasibility of yielding high quality. The $FeCl_3.6H_2O$ and $3-ft$ carbon column adsorption (either operated as fixed-bed or expanded-bed adsorber) was able to produce effluents of exceptionally high water quality having TOC< 3 *mg/L* and turbidity < 1 *JTU.*

Kaliniichuk et al. (1972) studied the treatment of petroleum refinery wastewaters by coagulation, using a mixture of ferric sulphate and chloride obtained by chlorinating a solution of ferrous sulphate. Amounts of the $Fe_2(SO_4)_3 + FeCl_3$ coagulant mixture used are in the range 64 – 166 *mg/L* and 100 – 250 *mg/L* based on the initial $FeSO_4.7H_2O$. Treatment of water by coagulation with regeneration of the coagulant sludge with sulphuric acid reduced the consumption of coagulant and the yield of coagulant sludge, and increases mineralization of the water only slightly while at the same time reducing the petroleum product content from 150 – 250 *mg/L* to 10 – 15 *mg/L*.

Saifutdinov et al. (1974) had given the information that wastewaters from the first sewer system in refineries ("industrial drain system"), before reuse in a circulating water system, should be given complete biochemical treatment and then post-treatment to remove the activated sludge. Design indices are proposed for the biochemical treatment and post-treatment of refinery "industrial drain water", along with standards for the circulating water quality when these effluents are completely reused. The reuse of biochemically treated "industrial drain water" instead of the mechanically treated effluent will permit a reduction in the rates of corrosion, scaling, and overgrowth in the circulating water, amounting to 34, 66, and 69%, respectively.

Grieves et al. (1977) had shown that adding powdered activated carbon to the aeration section of an activated sludge process is a viable alternative to a granular carbon column addition to a refinery wastewater treatment facility. The pilot plant studies were done and program was conducted in three phases. The first two phases were used to demonstrate enhancement with high doses of several carbons. Positive results from these phases gave incentive to a third phase, to investigate the addition of small amounts of the newly developed high surface area carbon to activated sludge units operated at high sludge age.

Burks (1982) has made a review of pollutants in petroleum refinery wastewater and its effect of aquatic environment. He found that in the past decade, the number of organic chemical contaminants identified in oil refinery wastewaters has risen from less than 20 to over 300. This increase in knowledge was made possible by advances in gas chromatography-mass spectrometry instrumentation and new techniques to maximize resolution of capillary chromatography. The contaminants in oil refinery wastewaters acutely lethal to aquatic organisms can be removed by biological treatment systems. However, biological treatment systems may not be capable of removing all deleterious contaminants. Long-term fathead minnow bioassays of biologically treated refinery wastewaters resulted in 10 – 50% mortality after 14 – 16 *days* of exposure. The lethal effects were eliminated by sequential treatment with dual media filtration-activated carbon adsorption.

Moursy and Abo El-Ela (1982) have got some findings which are here under. Refinery wastewater from Moustorod oil refinery, Cairo, Egypt, was treated by chemical coagulation. This step was followed by rapid solid-liquid separation using floatation under pressure of 4 *atm*. A floatation tank was designed for this purpose. Gas liquid chromatography was used for the determination and identification of hydrocarbon compounds in refinery wastewater. This treatment technique proved to be very promising for reducing the hydrocarbon compounds, as well as other pollutants, to a very low concentration. The results obtained shown that some of the hydrocarbons were completely removed.

Dalmacija et al. (1985) has done a study of the primary microbiological purification of mixed oil refinery and municipal wastewater using the active sludge process in a two-stage laboratory set-up. The advanced-secondary microbiological treatment of the mixed wastewaters was accomplished by using biologically active carbon. The highest total effect of the organic matter removal for both the primary and secondary microbiological treatment was achieved when the two wastewaters were mixed in the ratio 1:1, and it ranged from 97.7 – 99.22%. The organic matter load in the effluent expressed as BOD_5, was 0.3 – 5.7 mgO_2dm^{-3}. When conditions in the columns containing biologically active carbon were changed from aerobic into anaerobic ones, the denitrification bacteria were allowed to use the adsorbed organic matter as the substrate.

Yuan et al. (1991) gave the information that many refinery wastewater treatment plants have difficulties in satisfying their NPDES discharge limitations due to the operation and control problems of their activated sludge processes. Integrated expert systems are powerful tools to improve operation and control. It is demonstrated that an integrated expert system can help find operation problems, diagnose causes, and provide both qualitative and quantitative control advice to the operators. Process efficiency and reliability can be enhanced substantially.

Tyagi et al. (1993) has conducted a laboratory scale to assess the feasibility of a modified rotating biological contactor (RBC) with polyurethane foam (PUF) attached to the disks as porous support media to biodegrade petroleum refinery wastewater. Two parallel RBC-PUF units were operated simultaneously at different hydraulic loading rates [0.01, 0.02, 0.03, 0.04, 0.05 $m^3/(m^2.d)$] and at a rotational speed of 10 *rpm*. For all hydraulic loadings studied, the removal efficiencies of total COD and oil were above 87 and 80%, respectively. The results obtained in terms of biodegradation of COD, NH_3-N, phenol, hydrocarbons, and suspended solids in the modified RBC were generally better than conventional RBC.

Dalmacija et al. (1996) describes the possibility of application of a biosorption system with granulated activated carbon (GAC) for tertiary treatment of oil-field brine. In addition to the dissolved and dispersed oil, the oil field brine contained about 29 *g/L* of mineral matter, mainly NaCl. The investigation was carried out on two columns each containing 300 *g* of GAC. To form the bio film on GAC use was made of the micro-organisms from the setup for the purification of refinery wastewaters by activated sludge procedure. The wastewater flow rate through the columns was 40, 70, 95, and 130 *L/day*. It was found that the activated carbon in the columns was capable of removing 2.6 times more organic matter than was its adsorption capacity and its adsorption power was not thus exhausted. The procedure employed was very efficient-the organic matter content in the effluent did not exceed 2.5 *mg/L* (BOD_5).

Rao et al. (1999) has given a case study of Mathura refinery that it was commissioned during 1977 and effluent storage ponds were constructed at the same time. These storage ponds receive wastewater from the refinery at a rate of 10000 m^3/day. After treatment wastewater is discharged through a 3 *Km* pipeline to a stream leading to Yamuna River. The groundwater monitoring as well as water quality monitoring was carried at 24 observation wells in the refinery site during 1997. The water quality measurements indicated total dissolved chloride and sulphate concentration of native groundwater as 400 *mg/L*, whereas elevated levels up to 600 *mg/L* where found at the wells close to polishing ponds. Thus combined transport of chloride and sulphate was simulated in the mass transport model. A three-dimensional flow, path lines, and mass transport model of the aquifer system were constructed to analyze the impact of seepage from polishing ponds contaminating the groundwater regime. The permeability of aquifer varies between 1.5 – 2.5 *m/day*. The porosity of formation was assumed as 0.2. The constant head and the constant concentration boundaries were assigned to the nodes representing effluent storage ponds. The mass transport model was calibrated for twenty years by comparing total dissolved solids and sulphate concentration from 1997. The model prediction indicates further migration of contamination on the east of the effluent ponds in the future.

Teodosiu et al. (1999) focused on stabilizing the influence of process conditions for ultrafiltration, i.e. pressure, duration of fouling, frequency and duration of backwashing, and chemical cleaning on the rate of fouling and process efficiency. Two ultrafiltration membranes (made up of polyethersulphone/polyvinylpyrollidone), with same molecular weight cut-off (150000 D_a), but with different coatings were used. Experimental results shown that the A-LF (low fouling membrane) was easy to clean by backwashing or enhanced backwashing, having a better flux restoration and a higher frequency as production and operation than A membrane. Average removal efficiencies of 98% for turbidity and TSS and 30% for COD have been obtained, for ultrafiltration tests, irrespective of process conditions.

Bagajewicz (2000) presented a review of procedure to design and retrofit water networks. It was first shown that the problem has been decomposed into the design of two interacting sub-systems. One problem is the fresh water and wastewater reuse allocation and the other is the wastewater treatment problem. It is also shown that how the wastewater treatment problem was modeled as a distributed and decentralized treatment. The road map towards zero discharge and energy integrated solutions is then discussed. Several solution approaches are briefly outlined emphasizing the main trend leaning towards the use of mathematical programming. The major claim is that mathematical programming can produce globally optimal solutions and practically important sub-optimal solutions when conceptual insights are employed to build the models. Finally, a few of the existing challenges of the area are outlined.

Zbontar and Glavic (2000) analyzed technological wastewater streams in a refinery and petrochemical complex. Wastewater flow rate, temperatures, pH, and pollutant contents were measured. Regarding the characteristics of the individual waters, possible connections between water outflows from the processes or process units and potential water consumers were determined. Possibilities to reduce the flow rate of technological wastewater with wastewater reuse or preliminary regeneration and reuse were found. The consumption of fresh water could be lowered by 11.2 m^3/hr, reducing the treatment system load and prolonging its residence time by 7%.

Fratila Apachitei et al. (2000) proposed a treatment scheme comprising ultrafiltration (UF) and reverse osmosis (RO) for reuse of refinery and petrochemical effluent, high in turbidity and salinity, as cooling. UF tests were performed at constant transmembrane pressure (0.2 *bars*) using hollow fiber polyethersulphone membranes coated with polyvinylpyrolidone. UF membranes with two different molecular weight cut-offs (50 and 150 *kDa*) were compared. The two membranes performed very differently. An analysis of the blocking mechanisms could not explain the rapid drop in flux for the 150 *kDa* membrane as compared with the 50 *kDa* membrane, since a gradual change from complete to intermediate blocking and cake filtration was observed in both cases. However, a field emission scanning electron microscopy (FESEM) analysis of both UF membranes suggested that the superior filtration performance may be due to the highly interconnected pore system of the 50 *kDa* membrane, resulting in a '3D-bridge-type' surface morphology.

Rigas et al. (2000) has investigated that water resulting from the dewatering process of petroleum storage tanks was treated in a pilot separator to investigate the effectiveness of the combined action of a coagulant (aluminum sulphate) and a cationic flocculant. The simple one-stage air floatation system constructed combined with the central composite design of experiments, proved to be effective for studying the multi-variable effects of floatation and determining chemical doses. For the optimization parameters selected (turbidity, total suspended solids, and oil content reductions) optimal regions were found inside the variation intervals of the design factors. Further investigation of the system directs to higher alum and lower polyelectrolyte doses, provided the obtained results would not be satisfactory in an eventual industrial application. The effectiveness of the search method used offers the possibility to include some additional design factors in a new search for the optimum.

Sarathy et al. (2002) has done a survey of the process streams at an operating petroleum refinery and it showed that desalting water from the crude and splitter units had the highest concentrations of pollutants, and accounted for approximately one-third of the BOD and COD of the combined effluent. Combined effluent (BOD: 234 ± 62 *mg/L*, COD: *510* ± *0 mg/L*, and Microtox EC_{50} 4.9 ± 0.4%) was treated using a laboratory-scale batch biological reactor. 93% of BOD and 77% of COD were removed over the first 24 *hrs* of biological treatment. Acute (Microtox) toxicity was reduced in two discrete stages; the first coinciding with BOD and COD removal and the second stage occurring after BOD and COD had been removed. A final EC_{50} value of 27.8% was achieved in batch tests.

Moreno et al. (2002) investigated constructed vertical macrophyte systems, for nitrogen removal from oil refinery wastewater. Detailed studies were carried out in laboratory columns (diameter, 0.06 *m*; depth, 0.5 *m*; operating volume, 0.6 *L*) planted with common reed, *Phragmites australis.* Through a vertical flow format, collected oil refinery wastewater was supplied directly to the columns. Wastewater quality varied through the experimental period with initial ammonia concentrations ranging from 3 – 20 *mg* N/*L*. Effective ammonia removal was obtained for the planted columns with a hydraulic detention time of 5 *hr*. Removal efficiencies above 90% was obtained for high (above 6 *mg* N/*L*) ammonia inflow concentrations. A satisfactory ammonia removal was obtained at shorter detention times for the low initial concentrations.

Zhong et al. (2003) studied and investigated the treatment of oily wastewater produced from post-treatment unit of refinery processes using flocculation and micro-filtration with zirconia membrane. The results show that the oil content and COD value were decreased dramatically by flocculation, and the optimum flocculant is 3530S which is a derivative of polyacrylamide. The influence of flocculation conditions on flocculation results is also investigated by orthogonal experiments, and the optimum conditions are dosage of 70 *mg/L*, temperature of $40^{O}C$, stirring time and holding time of 90 *min* each. The results of filtration test show that the membrane fouling decreased and the permeate flux and permeate quality increased with flocculation as pretreatment. The permeate obtained from flocculation and micro-filtration can meet the National Discharge Standard and the recommended operation conditions for pilot and industrial application are transmembrane pressure of 0.11 *MPa* and cross-flow velocity of 2.56 *m/sec*.

Bhattacharya (2003) has given an Indian scenario of treatment and disposal of refinery sludges. Various types of pollutants like phenols, heavy metals, etc., are present in the sludges and they are treated as hazardous waste. Oily sludge, which is generated in much higher amount compared to other sludges, contains phenol (90 – 100 *mg/Kg*), nickel (17-25 *mg/Kg*), chromium (27 – 80 *mg/Kg*), zinc (7 – 80 *mg/Kg*), manganese (19 –

24 *mg/Kg*), cadmium (0.8 – 2.0 *mg/Kg*), copper (32 – 120 *mg/Kg*) and lead (0.001 – 0.12 *mg/Kg*). Uncontrolled disposal practices of sludges in India cause degradation of environmental and depreciation of aesthetic quality. Environmental impact due to improper sludge management has also been identified. A ranking exercise has been carried out to evaluate the alternatives and select the appropriate one. A detailed design of the selected waste management system has been presented.

Rajkumar and Palanivelu (2004) presented the results of phenolic compounds containing wastewater generated from oil refineries by electrochemical method. Experiments were conducted at a fixed current density of 5.4 A/dm^2 using Ti/TiO_2-RuO_2-IrO_2 electrode and an undivided reactor. During the various stages of electrolysis, parameters such as COD and TOC concentrations were determined in order to know the feasibility of electrochemical treatment. Adsorbable organic halogens (AOX) were detected at high concentrations during the electrolytic treatment of the effluents. The present study proves the effectiveness of electrochemical treatment for highly concentrated bio-refractory organic pollutants present in the industrial wastewater.

Lee (2004) designed and used a two-stage sequencing batch reactor (SBR) system for treatment of oily wastewater with COD and oil and grease (O and G) concentrations ranging from 1722 – 7826 and 5365 – 13350 *mg/L*, respectively. A suitable start-up protocol was developed using gradual increase in oily wastewater composition with methanol as the co-substrate. This strategy enabled a short acclimation period of 12 *days* for the sludge in the two-stage SBR to adapt to the oily wastewater. After acclimation, the 1st stage and 2nd stage SBRs were able to achieve COD removals of 47.0 ± 2.4 and 95.3 ± 0.5%, respectively. The 1st stage SBR was able to achieve 99.8 ± 0.1% of oil and grease removal and effluent oil and grease from the 1st stage SBR was only 6 ± 2 *mg/L*. The 2nd stage SBR was used to further remove COD in the effluent from the 1st stage SBR. The final effluent from the 2nd stage SBR had a COD concentration of 97 ± 16 *mg/L* with no detectable oil and grease content. Thus, a two-stage SBR system was shown to be feasible for treating high strength oily wastewater to meet the local discharge standards.

Jianping et al. (2005) has carried out aerobic treatment of wastewater in 200 dm^3 gas-liquid-solid three-phase flow air lift bioreactor, in which a biological membrane replaced the activated sludge. The influence of temperature, pH, gas-liquid ratio, and HRT on the reduction in COD and NH_4-N were discussed here. The optimum operation conditions were obtained at a temperature of $25\text{-}35^{O}C$, pH value of around 7.0 – 8.0, gas-liquid ratio of 50 and HRT of 4 *hrs.* Under optimum operating conditions, the effluent COD and NH_4-N were less than 100 and 15 mg/dm^3, respectively for more than 40 *days*, satisfying the National Primary Discharge Standard of China.

Vaiopoulou et al. (2005) presented an alternative flowchart for the biological removal of hydrogen sulphide from oil-refining wastewater and pilot-scale plant was fed with a mixture of the following constituents: (a) original wastewater from oil refining industry, (b) the effluent of the existing nitrification-stage treatment plant, and (c) sulphide in the form of Na_2S. Anoxic sulphide to sulphate oxidation, with nitrate as a terminal electron acceptor, proved very successful, as incoming concentrations of 110 *mg* S^{2-}/L were totally converted to SO_4^{2-}. At complete denitrification, the concentration of S^{2-} in the reactor effluent was less than 0.1 *mg/L*. This alternative new treatment scheme was further introduced at the refinery's wastewater processing plant. Thus, complete H_2S removal is now accomplished by the combination of the proposed biological method and the existing stripping with CO_2. As a result, stripping, and thus its cost, is reduced by 70%.

Andreev (2006) discussed the exhaustive local treatment of refinery effluents with single-tower scheme to remove hydrogen sulphide and ammonia in primary oil refinery units. The local treatment with the single tower scheme is conducted with two methods which includes desorption with hydrocarbon gas or water vapour for hydrogen sulphide and ammonia and heterogenic catalytic method for sulphide sulphur. The hydrogen sulphide and ammonia desorbed by the water vapour are delivered to process unit furnaces, which increases the amount of atmospheric emissions of harmful substances. Heterogenous-catalytic treatment of condensate to remove sulphide sulphur consists of oxidation of toxic sulphides with atmospheric oxygen in the presence of a catalyst into less toxic thiosulphates. The removal of sulphates is required for using the treated condensates in refinery's closed water supply system and also for the biological pretreatment.

Barrios-Martinez et al. (2006) shown the feasibility of the MBR treatment of a synthetic effluent containing a large amount of phenol since phenol and their derivatives are widely used as raw material in oil refineries. Using a biomass acclimated to phenol degradation, the critical conditions of membrane separation were determined: TMP = 100 *kPa* (1 *bar*) and $v = 5$ *m/sec*. In these conditions, the permeate flux remained constant and high with a permeability about 10^{-3} $Lh^{-1}\ m^{-2}\ Pa^{-1}$ (100 $Lh^{-1}\ m^{-2}\ bar^{-1}$). The experiment of phenol degradation proved the effectiveness of the step of activated sludge acclimation, since a steady state was reached in a few hours. No phenol was detected in the permeate although a large quantity of phenol (50 *g/day*) was degraded. The absence of suspended matter, removal of a substantial amount of phenol, and a good performance on organic substance removal shows the excellent performances of MBR.

Coelho et al. (2006) investigated the performance of several oxidation processes to remove organic pollutants from sour water. Preliminary experiments were conducted, using the following processes: H_2O_2, H_2O_2/UV, UV, photocatalysis, ozonation, Fenton and photo-Fenton. All processes, except Fenton and photo-Fenton, did not lead to satisfactory results, reducing at most 35% of the sour water dissolved organic carbon (DOC). Batch experiments revealed that the Fenton reaction is very fast and reaches in a few minutes, an ultimate DOC removal of 13 – 27%, due to the formation of iron complexes. Radiation for an additional period of 60 *min* can increase DOC removal up to 87%. Experiments were also conducted in a continuous mode; operating one 0.4 *L* Fenton stirred reactor and one 1.6 *L* photo-Fenton reactor in series. DOC removals above 75% were reached, when the reaction system was operated with HRT higher than 85 *min*.

CHAPTER 5

DESIGN OF HYBRID INTEGRATED EFFLUENT TREATMENT SYSTEM

4.0 DESIGN EQUATIONS

4.0.0 API SEPARATOR DESIGN EQUATIONS

Equations that are used in the design of API Separator are here under:

$$V_T = \left[\frac{g * D_P^2 * \left(\rho_W - \rho_O \right)}{18 * \mu} \right] \qquad \ldots(1)$$

where,

μ = Absolute viscosity of wastewater
g = Acceleration due to gravity
V_T = Vertical velocity/rise rate of design oil globule
ρ_W = Density of water
ρ_O = Density of oil
D_P = Diameter of oil globule which is to be separated or removed

$$V_H = V_T * 15 \qquad \ldots(2)$$

where, V_H = Horizontal velocity

$$V_H \leq 3\,fpm \qquad \ldots(3)$$

$$A_C = \frac{Q_M}{V_H} \qquad \ldots(4)$$

where,

A_C = Minimum vertical cross – sectional area
Q_M = Design flow to separator
V_H = Horizontal Velocity

$$n = \frac{A_C}{14.84\,m^2} \qquad \ldots(5)$$

where, n = Number of separator channels

$$d = \frac{A_C}{B * n} \qquad \ldots(6)$$

where, B = Channel width

- *Necessary and sufficient conditions:*

  - $0.3 < \frac{d}{B} < 0.5$ ...(7)
  - $d = 3 - 8\,feet$ ...(8)

$$L = F * \left(\frac{V_H}{V_T}\right) * d \qquad \text{...(9)}$$

where,

L = Length of channel
F = Turbulence and short – circuiting factor
V_H = Horizontal velocity
(V_T) = Vertical velocity of design oil globule
d = Depth of channel

4.0.0 Corrugated Plate Interceptor Design Equations

$$A_P = \left(\frac{Q_M}{V_T}\right) \qquad \text{...(10)}$$

where,

Q_M = Design flow $\left(in\ \frac{m^3}{hr}\right)$
A_P = Projected surface area of the plates, m^2
A_A = Actual Plate area
V_T = Vertical velocity (calculated by equation 1)

$A_{P1} = A_P * 1.1$ (as 10% of over design plate surface area is given) ...(11)

$$A_A = \left(\frac{A_{P1}}{Cos\ 45^O}\right) \qquad \text{...(12)}$$

- *Necessary and sufficient conditions that are required in the design of CPI Separator:*
  - $500 \le Re \le 2000$ ...(13)
  - d (Plate spacing) $\approx 2 - 4\ cm$ ...(14)

$$\upsilon = \left(\frac{\mu}{\rho}\right) \qquad ...(15)$$

where,

υ = Kinematic viscosity
μ = Viscosity of wastewater
ρ = Density of wastewater

$$L = \left(\frac{\upsilon * \text{Re} * \sqrt{2}}{2 * V_T}\right) \qquad ...(16)$$

where,

L = Length of the separator
Re = Reynolds number
V_T = Vertical velocity (calculated by equation 1)

[This formula is obtained from "**Designing Parallel Plate Separators**", Chemical Engineering, 1977, Volume 84, pp. 105 – 107 by **J. G. Miranda**]

$$N_P = \left(\frac{A_A}{W_P * L_P}\right) \qquad ...(17)$$

where,

N_P = Number of plates
A_A = Actual plate are (calculated in equation 12)

4.0.0 Dissolved Air Flotation System Design Equations

$$\frac{A}{S} = \frac{1.3 * s'_a * (f * P - 1) * Q_R}{(S_I * Q)} \qquad ...(18)$$

where,

A = volume of air (in *mL*)
S = mass of solids (in *mg*)
s'_a = solubility in air (in *mL/L*)
S_I = Influent suspended solids
Q = mixed liquor flow $\left(\frac{m^3}{hr}\right)$
f = fraction of air dissolved at pressure P (in *atm*)
P = operating temperature (in *atm*)

[Where, $P=\left(\dfrac{p+101.35}{101.35}\right)$, p = gage pressure (in *kPa*)]

Q_R = pressurized recycle flow $\left(\dfrac{m^3}{hr}\right)$

$$A_r=\left(\frac{Q+Q_R}{SLR}\right) \qquad \ldots(19)$$

where,

A_r = Surface area, m^2

SLR = Surface loading rate, $\left(\dfrac{gpm}{ft^2}\right)$

$$V=(Q+Q_R)*(Detention Time) \qquad \ldots(20)$$

where,

V = Volume of the tank.

$$d=\left(\frac{V}{A_R}\right) \qquad \ldots(21)$$

where,

d = Depth of the tank

V = Volume of the tank (calculated from equation 20)

A_R = Surface area (calculated from equation 19)

$$Solid\ loading\ rate=\left\{\frac{(Initial\ Concentration)*(Corrected\ Q_M)}{A_R}\right\} \qquad \ldots(22)$$

4.0.0 Sequencing Batch Reactor and Membrane Bioreactor Design Equations

$$\frac{bpCOD}{pCOD}=\frac{\left[\left\{\dfrac{bCOD}{BOD}\right\}*(BOD-sBOD)\right]}{[COD-sCOD]} \qquad \ldots(23)$$

$$(nbVSS)=\left[1-\left(\frac{bpCOD}{pCOD}\right)\right]*VSS \qquad \ldots(24)$$

$$(iTSS)=(TSS_o)-(VSS_o) \qquad \ldots(25)$$

$$T_C=t_F+t_A+t_S+t_D+t_I \qquad \ldots(26)$$

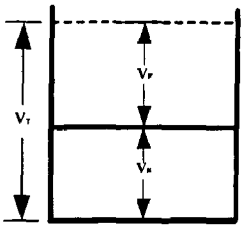
$$t_S=t_A+t_S+t_D \qquad \ldots(27)$$

$$\text{Fill volume per cycle} = \left(\frac{\textit{Volumetric Flow Rate}}{\textit{Total Number of Cycle per Day}}\right) \quad \text{...(28)}$$

Develop mass balance based on solids in the reactor

Mass of solids at full volume = Mass of settled solids

i.e. $V_T * X = V_S * X_S$ ...(29)



where,

V_T = Total volume, m^3

V_S = Settled volume after decant, m^3

X_T = MLSS concentration at full volume, g/m^3

X_S = MLSS concentration in settled volume, g/m^3

$$\frac{V_S}{V_T} = \frac{X}{X_S} \quad \text{...(30)}$$

$$\textit{Sludge volume index (SVI)} = \frac{\left[\textit{Settled volume}\left(\frac{mL}{L}\right)*10^3\left(\frac{mg}{g}\right)\right]}{\textit{Suspended Solids}\left(\frac{mg}{L}\right)} \quad \text{...(31)}$$

To calculate fill fraction,

$$V_S + V_F = V_T \rightarrow \frac{V_S}{V_T} + \frac{V_F}{V_T} = \frac{V_T}{V_T} \rightarrow \frac{V_F}{V_T} = 1 - \frac{V_S}{V_T} \quad \text{...(32)}$$

$$\frac{V_F}{V_T} = 0.3 \rightarrow \mathrm{V_T} = \frac{\left(\frac{V_F}{Tank}\right)}{0.3} \quad \text{...(33)}$$

$$\textit{Hydraulic retention time}, \tau = \left[\frac{\left(\frac{V_T}{Tank}\right) * (\textit{Number of Tanks})}{\textit{Volumetric Flow Rate}}\right] \quad \text{...(34)}$$

To determine SRT, the following formulae are used:

$$\left(P_{X,VSS}\right) = \frac{Q*Y*(S_o-S)*\left(\frac{1kg}{10^3 g}\right)}{1+(k_d)*SRT} + \frac{Q*Y*(S_o-S)*(f_d)*(k_d)*SRT*\left(\frac{1kg}{10^3 g}\right)}{1+(k_d)*SRT}$$

(A) (Heterotrophic biomass) (B) (Cell biomass)

$$+\frac{Q*Y_n*(NO_X)*\left(\frac{1kg}{10^3 g}\right)}{1+(k_{dn})*SRT} + Q*(nbVSS)*\left(\frac{1kg}{10^3 g}\right) \qquad ...(35)$$

(C) (Nitrifying bacteria) (D) (Non-biodegradable VSS in effluent)

where,

NO_X = Concentration of NH_4-N in the influent flow that is nitrified, $\frac{mg}{L}$

K_{dn} = Endogenous decay coefficient for nitrifying organism $\left(\frac{gVSS}{gVSS * Day}\right)$

Total mass of dry solids wasted per day include total suspended solids (TSS) and not only volatile suspended solids (VSS). TSS includes VSS + Inorganic solids. Inorganic solid in wastewater (TSS – TSS_O) contribute to inorganic solids and are additional biomass production term that must be added to equation (A)

Biomass term in the equation (A) containing inorganic solid and VSS. Fraction of total biomass is about 0.85, based on cell concentration (Table 7-4). Therefore, equation (A) can be modified as follows to calculate solid production in terms of TSS.

$$\therefore \quad P_{X,TSS} = \frac{A}{0.85} + \frac{B}{0.85} + \frac{C}{0.85} + D + Q*\left(TSS - TSS_o\right) \qquad ...(36)$$

where,

Q = Inert TSS in influent

TSS = Influent wastewater TSS concentration

TSS_O = Influent wastewater VSS concentration

Equation (C) can be represented as:

$$Oxygen\,used = bCOD\,removal - COD\,of\,waste\,sludge \qquad ...(37)$$

Multiply equation (37) by SRT, we have:

$$\left(P_{X,TSS}\right)*SRT = \frac{Q*Y*\left(S_O-S\right)*SRT}{\left\{1+k_d*\left(SRT\right)\right\}*0.85} + \frac{Q*Y_n*(NO_X)*SRT}{\left[1+(k_{dn})*SRT\right]*0.85} + Q*(nbVSS)*SRT$$

$$+Q*\left(TSS-TSS_O\right)*SRT + \frac{Q*Y*(S_o-S)*(f_d)*(k_d)*SRT^2}{\left[1+(kd)*SRT\right]*0.85} \quad \ldots(38)$$

$$\left(P_{X,TSS}\right)*SRT = \left(V_T*X_{MLSS}\right) \quad \ldots(39)$$

$$k_D(atT^OC)=k_D\,(at20^O\,C)*\left(\theta\right)^{T-20} \quad \ldots(40)$$

$$k_{DN}(atT^OC)=k_{DN}\,(at20^O\,C)*\left(\theta\right)^{T-20} \quad \ldots(41)$$

$$\left(V_T*X_{MLSS}\right) = \frac{Q*Y*(S_o-S)*SRT}{\left\{1+(kd)*SRT\right\}} + \frac{Q*Y*(S_o-S)*(f_d)*(k_d)*SRT^2}{\left[1+(kd)*SRT\right]}$$

$$+\ Q*(nbVSS)*SRT + \frac{Q*Y_n*(NO_X)*SRT}{\left[1+(k_{dn})*SRT\right]} = \left(P_{X,VSS}\right)*SRT \quad \ldots(42)$$

Amount of $NH_4 - N$ oxidized (NO_X)

By making nitrogen balance:

[Nitrogen oxidized] = [Nitrogen in influent] – [Nitrogen in effluent] – [Nitrogen in Cell tissues] ...(43)

$$Q*\left(NO_X\right)=Q*\left(TKN_O\right)-Q\left(N_E\right)-0.12*\left(P_{X,BIO}\right)$$

$$\left(NO_X\right)=\left(TKN_O\right)-\left(N_E\right)-0.12*\frac{P_{X,BIO}}{Q} \quad \ldots(44)$$

$\left(P_{X,BIO}\right)$ = [Items A + B + C of Equation (35)]

$$\left(P_{X,BIO}\right) = \frac{Q*Y*(S_o-S)}{\left\{1+(kd)*SRT\right\}} + \frac{Q*Y_n*(NO_X)}{\left[1+(k_{dn})*SRT\right]}$$

$$+\frac{Q*Y*(S_o-S)*(f_d)*(k_d)*SRT}{\left[1+(kd)*SRT\right]} \quad \ldots(45)$$

$$Initial\,concentration,\ N_O=\left(\frac{Total\,oxidizable\,Nitrogen\,at\,beginning}{V_T}\right) \quad \ldots(46)$$

To calculate react time

$$K_N*\ln\left(\frac{N_O}{N_T}\right)+\left(N_O-N_T\right)=X_N*\left(\frac{\mu_{MN}}{Y_N}\right)*\left(\frac{DO}{DO+K_O}\right)*t \quad \ldots(47)$$

(i) Nitrifier concentration, $X_N = \frac{[Q*Y_n*(NO_X)*SRT]}{[1+(k_{dn})*SRT]*V_T}$ ...(48)

(ii) $\mu_{MN}(at\,T^OC)=\mu_{MN}(at\,20^OC)*(\theta)^{T-20}$ ...(49)

(iii) $K_N(at\,T^OC)=K_N(at\,20^OC)*(\theta)^{T-20}$ ...(50)

$$Decant\ pumping\ rate=\left[\frac{\left(\frac{Fill\ volume}{Cycle}\right)}{Decant\ time}\right] \quad ...(51)$$

Oxygen required per tank: $R_O=Q*(S_O-S)+4.33*Q*(NO_X)-1.42\,P_{X,BIO}$ ...(52)

$$Average\ oxygen\ transfer\ rate=\left(\frac{Oxygen\ required\ per\ Tank}{Total\ aeration\ time}\right) \quad ...(53)$$

Sludge production, $(P_{X,TSS})=\frac{V_T*(X_{TSS})}{SRT}$ ...(54)

Observed yield, $\frac{g\,TSS}{g\,BOD}=\left[\frac{(P_{X,TSS})}{BOD\ removed}\right]$ ...(55)

Observed yield, $\frac{g\,VSS}{g\,BOD}=\left[\frac{(P_{X,TSS})}{BOD\ removed}\right]*\left(\frac{X_{MLVSS}}{X_{MLSS}}\right)$ ...(56)

Observed yield, $\frac{g\,TSS}{g\,bCOD}=\left[\frac{(P_{X,TSS})}{bCOD\ removed}\right]$ ...(57)

$\left(\frac{F}{M}\right)$ Ratio $=\left(\frac{kg\,BOD}{Kg\,MLVSS*day}\right)=\left(\frac{Q*S_O}{X*V}\right)$ ...(58)

$L_{ORG}=\frac{kg\,BOD}{m^3*day}=\left(\frac{Q*S_O}{V}\right)$ ...(59)

Table 12: Activated Sludge Kinetic Coefficients for Heterotrophic Bacteria at $20^{O}C$

Coefficient	Unit	Range	Typical value
μ_m	g VSS/(g VSS * day)	3.0 – 13.2	6.0
K_S	g bCOD/m3	5.0 – 40.0	20.0
Y	g VSS/g bCOD	0.30 – 0.50	0.40
k_d	g VSS/(g VSS * day)	0.06 – 0.20	0.12
f_d	Unit less	0.08 – 0.20	0.15
θ values			
μ_m	Unit less	1.03 – 1.08	1.07
k_d	Unit less	1.03 – 1.08	1.04
K_S	Unit less	1.00	1.00

Table 13: Activated Sludge Nitrification Kinetic Coefficients at $20^{O}C$

Coefficient	Unit	Range	Typical value
μ_{mn}	g VSS/(g VSS * day)	0.20 – 0.90	0.75
K_n	g bCOD/m3	0.50 – 1.0	0.74
Y_n	g VSS/g bCOD	0.10 – 0.15	0.12
k_{dn}	g VSS/(g VSS * day)	0.05 – 0.15	0.08
K_O	Unit less	0.40 – 0.60	0.50
θ values			
μ_{mn}	Unit less	1.06 – 1.123	1.07
K_{dn}	Unit less	1.03 – 1.08	1.04
K_n	Unit less	1.03 – 1.123	1.053

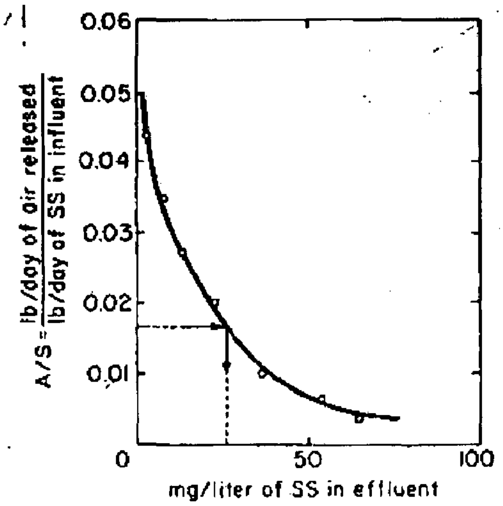


Figure 12: Typical Correlation of Parameter (A/S) vs. Concentration of Suspended Solids in Effluent.

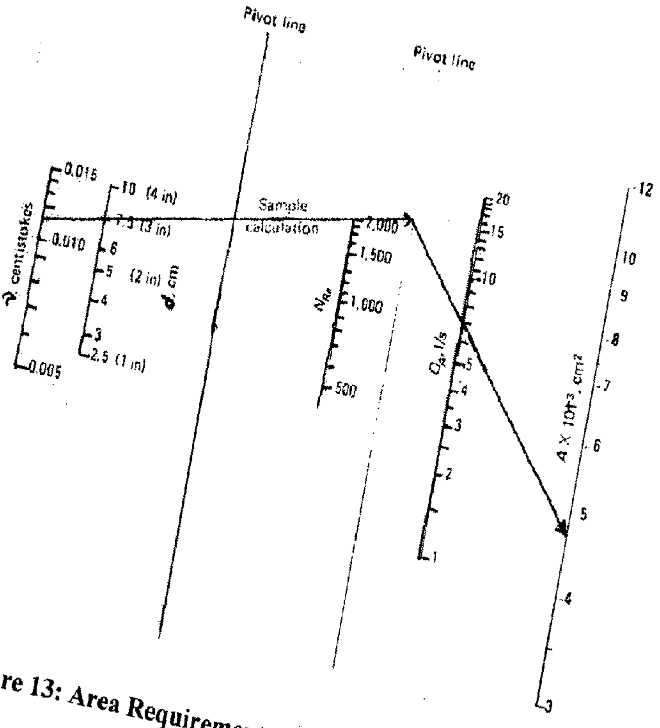


Figure 13: Area Requirement to Ensure Laminar Flow.

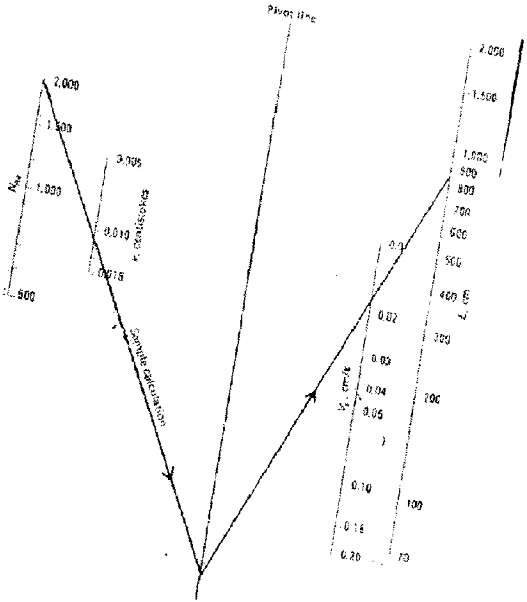


Figure 14: Separator Length to Remove Oil Globules.

5.2 DESIGN OF API SEPARATOR

Unit Design Data

Design flow, Q_m	$150\frac{m^3}{hr}$
Temperature, T	$43^O C$
Specific gravity of water (S_w)	1
Specific gravity of oil (S_o)	0.875
Viscosity of oily water (99% Water + 1% Oil)	$1\ cP$
Diameter of oil particles to be separated, D_p	$150\ \mu m$

Note: Maximum amount of oil (95%) are having the particle size of around $150\ \mu m$

(1) Calculation of Globule Rising Velocity (V_T)

By equation (1)

$$\mu = 1\ cP = 1 * 10^{-2} P = 1 * 10^{-3} \frac{kg}{m * \sec} = 1 * 10^{-3} * 3600 \frac{kg}{m * hr}$$

$$\therefore \quad V_T = \left[\frac{9.81 * (3600)^2 * (150 * 10^{-6})^2 * (1000 - 875)}{18 * 10^{-3} * 3600}\right] \frac{m}{hr} \rightarrow V_T = 5.52 \frac{m}{hr}.$$

$\therefore$ Globule Rising Velocity $(V_T) = 5.52 \frac{m}{hr}$.

(2) Calculation of Horizontal Velocity *(V_H)*

The design mean horizontal velocity is defined by:

By equation (2)

$$\therefore \quad V_H = 15 * 5.52 \frac{m}{hr} = 82.80 \frac{m}{hr} = 4.53\, fpm$$

Here, $4.53\, fpm > 3\, fpm$ [As per condition mentioned in equation (3)]

So, a horizontal velocity *(V_H)* of $3\, fpm$ or $5.52 \frac{m}{hr}$ is used because this is the maximum recommended mean horizontal velocity.

(3) Calculation of Minimum Vertical Cross - Sectional Area *(A_C)*

The minimum vertical cross – sectional area is calculated using the equation (4):

$$\therefore \quad A_C = \frac{150 \frac{m^3}{hr}}{54.86 \frac{m}{hr}} \rightarrow A_C = 2.734\ m^2.$$

(4) Calculation of No: of Separator Channels (n)

Maximum cross – sectional area for single channel is taken as:

$20\,feet * 8\,feet = 160\,feet^2 = 14.864\ m^2$

Number of separator channels is calculated by the following equation (5):

$$\therefore \quad n = \frac{2.73\,m^2}{14.84\,m^2} \rightarrow n = 0.2 \approx 2$$

Fractional no: of channels are rounded up to the next whole no: and n must be greater than or equal to 2, so this value is acceptable.

∴ Number of separator channels (n) are taken as 2.

(5) Calculation of Channel Width (B) and Depth (d)

The channel depth is calculated by the following equation (6):

Here for the sake of calculation the channel width is taken as $B = 20\,feet = 6.1\ m$.

Necessary and sufficient conditions are given in equation (7) and (8), respectively. The value of channel width (B) must range in between $6 - 20\,feet$ ($1.83 - 6.1\ m$).

Table 14: Calculation of Exact values of Depth (d) and Channel Width

Channel Width (B) [in m]	**Channel Depth (d) [in m]**	$\left(\frac{d}{B}\right)$ **ratio**
6	0.23	0.038
5	0.273	0.05
4	0.340	0.085
3	0.455	0.15
2.5	0.550	0.22
2.4	0.570	0.24
2.3	0.60	0.26
2.2	0.63	0.29
2.1	**0.65**	**0.31**
2.0	0.69	0.34
1.9	0.72	0.38
1.8	0.76	0.42

So, with the given configuration we have came to the conclusion that the values are described here under:

Number of Separator Channel = 2

Channel Width $(B) = 2.1\ m$

Channel Depth $(d) = 0.7 \approx 1\ m$

$\left(\frac{d}{B}\right)$ Ratio $= 0.48 \approx 0.5$

(6) Calculation of Separator Length *(L)*

Since separator depth *(d)* and Separator width *(B)* is calibrated or determined, the final dimension, i. e. the channel length *(L)* is obtained by using the following equation (9):

With $\left(\frac{V_H}{V_T}\right) = \left(\frac{54.86}{5.51}\right) = 9.96$, the value of F is calculated by:

$\frac{V_H}{V_T}$	**Turbulence Factor** (F_T)	$F = 1.2*(F_T)$
10	1.27	1.52
6	1.14	1.37
9.96	**1.269**	**1.523**

By putting the values of F, $\frac{V_H}{V_T}$, d we will get the value of separator length

$$L = (1.523 * 9.96 * 1)\ m = 15.2\ m \approx 16\ m$$

A check is performed to determine that $\frac{L}{B}$ is greater than or equal to 5.

Here in this case, $\frac{L}{B} = \frac{16}{2.1} = 7.62$

$\because \quad \frac{L}{B} = 7.62 > 5$, so the design is satisfactory.

Separator configuration resulting from the following design data sheet consists of two-channels, each of 16 *m* long and 2.1 *m* wide and a water depth of 1 *m* plus desired freeboard.

Ancillary equipments:

(i) Oil skim pipes: A good part of oil will separate in the inlet flume ahead of the flow distribution baffles, two retention baffles and skim pipes were provided. One is located ahead of the flow baffles and one is ahead of the effluent overflow weir. The distance between the two baffles and skims is 16 *m*.

API recommends a 10 *inch* (0.254 *m*) pipe for runs less than 12.5 *m* and thus larger pipes for longer runs. So 12 *inch* pipe or 1 *foot* pipe (0.3048 *m*) skim pipes are provided.

(ii) Oil sump: The influent contains 20000 *ppm* of oil and the effluent contains 1475 ppm of oil, the removal of oil is around 18525 *ppm*.

$$\text{Oil removal} = \left(18525 * 10^{-6}\right) * 150\ \frac{m^3}{hr} = 2.78\ \frac{m^3}{hr} \approx 3.0\ \frac{m^3}{hr}\ \text{of Dry oil.}$$

Assume that oil skim pipes remove 4 times as much water as oil; the flow into the sump is around $15 \frac{m^3}{day}$ of oil with 25% of oil.

Choosing a sump of 2.5 *m* * 2.5 *m* in plan, the required depth to store day's collection is:

$$\text{Plan area} = 2.5 * 2.5\ m^2 = 6.25\ m^2$$

$$\text{Liquid depth} = \frac{15}{6.25} = 2.4\ m$$

(iii) Oil retention baffles: The API recommended that oil retention baffles be submerged 0.5 – 0.6 of the liquid depth.

Depth of oil retention baffles = (0.6) * 1 *m* = 0.6 *m* or 1.97 *feet* or around 2 *feet.*

The baffles were made 3 *feet* or 0.9 *m* high. Thus they extend 1 *foot* above the normal liquid level.

(iv) Effluent weir: The weir top is a metal plate installed so that the weir height can be adjusted. This is required in order to have some means for providing a level weir. The outface of the weir is sloped to minimize any turbulence or frothing that might be caused by excessive free fall. The API recommends the maximum free fall be no more than 5 *feet.* The outfall box was provided with a floor 1 *foot* lower than the main separator floor. This allows the back up of a liquid level head of about 2 *feet* due to frictional resistance to flow in the effluent line.

(v) Distribution baffles: It is important to provide some types of vertical baffles at the inlet of the separator channels for the purpose of distributing the flow properly.

The API recommends either V - shaped slot baffles or pipes. For the installation, 3 - 4 *inch* (0.08 - 0.1 *m*) pipes were used so as to assure sufficient rigidity. The API recommends the slot open area be about 3 – 7% of the chamber cross – sectional area.

The API has recommended that the slots shouts be no less than $\frac{1}{8}$ wide to avoid plugging and to facilitate cleaning.

So, with 3 *inch* pipes on, and $3\frac{13}{16}$ *inch* pitch along with 0.25 *inch* slot width. If we take 20 pipes then there will be 21 slots provided. Thus,

$$\text{Open area} = 21 * (0.25 * 0.0254) * 1 = 0.1334\ m^2$$
$$= 13.34\%\ \text{of cross – sectional area.}$$

SUMMARY OF THE API SEPARATOR DESIGN:

Globule Rising Velocity (V_T)	$5.52\ \frac{m}{hr}$
Maximum recommended mean horizontal velocity (V_H)	$54.86\ \frac{m}{hr}$
Minimum vertical cross – sectional area, A_C	$2.734\ m^2$
Number of separator channels	2
Channel Width, B	2.1 *m*
Channel Depth, d	$0.7 \approx 1\ m$
$\left(\frac{d}{B}\right)$ Ratio	$0.48 \approx 0.5$
Length of the Separator, L	$15.2\ m \approx 16\ m$

Ancillary Equipments:

Oil Sump size	2.5 *m* * 2.5 *m* * 2.4 *m*
Oil skim pipes	12 *inch* pipe
Oil retention baffles width	0.9 *m*
Distribution baffles	20 pipes with 0.635 m (21 slots)
% Open area	13.34%

5.3 DESIGN OF CORRUGATED PLATE INTERCEPTOR (CPI)

Unit Design Data

Influent characteristics

Total Oil	$1475 \frac{mg}{L}$
Specific gravity of oil	0.9
Specific gravity of wastewater effluent	1 (99% water + 1% oil)
Viscosity of the effluent, μ	$1\ cP$
Diameter of the oil globule, D_P	$60\ \mu m$
Treated effluent characteristics	
Total oil	$55 \frac{mg}{L}$
Design removal efficiency	95% (minimum)
Flow rate	$300 \frac{m^3}{hr}$
Type of plates	Corrugated
Type of flow	Countercurrent

(1) Calculation of vertical oil rising velocity (V_T)

Vertical oil rising velocity is calculated by equation (1):

$$V_T = \left[\frac{9.81\left(\frac{m}{\sec^2}\right) * \left\{(60 * 10^{-6})^2 m^2\right\} * \left\{(1000-900)\frac{kg}{m^3}\right\}}{18.* 1 * 10^{-3} \frac{Kg}{m * \sec}} \right]$$

→ $V_T = 1.962 * 10^{-4} \frac{m}{\sec} = 0.706 \frac{m}{hr}$.

(2) Calculation of area (A_P)

Area is calculated here under as per the equation (10):

$$\therefore \quad A_P = \left(\frac{300 \frac{m^3}{hr}}{0.706 \frac{m}{hr}} \right) = 425\ m^2.$$

By equation (11) and (12), we have

→ $A_{PI} = 425 * 1.1 = 467.50\ m^2$ (10% of over design plate surface area is given)

→ $A_A = \left(\frac{467.5}{Cos\, 45^O} \right) = 665\ m^2$

Equation (13) and (14) presents the necessary and sufficient conditions that are required in the design of TPI Separator.

Assume a Reynolds no: of around 2000 and spacing in between the plates of around 2.0 *cm*.

Kinematic viscosity is calculated by the equation (15)

$$\therefore \quad \upsilon = \left[\frac{1 * 10^{-2} \dfrac{gm}{cm * \sec}}{0.9 \dfrac{gm}{cm^3}} \right] \rightarrow \upsilon = 0.0111 \frac{cm^2}{\sec} \rightarrow \upsilon = 0.0111 * 10^{-4} \frac{m^2}{\sec}.$$

Equation (16) shows the formula to calculate length of the separator (L).

$$\therefore \quad L = \left[\frac{1.11 * 10^{-6} \left(\dfrac{m^2}{\sec} \right) * 2000 * 3600 * \sqrt{2}}{2 * 0.706 \left(\dfrac{m}{hr} \right)} \right] \rightarrow L = 8.02\ m = 26.3\, feet \approx 27\, feet.$$

If we calculate the length with the help of Figure no: 14 we will get the length of separator is around 8.00 *m*.

Let us take a width of 2.75 *m*. [It is taken from the data www.natcogroup.com, for a given flow rate for a desired removal of oil this width is taken.]

Number of plates is calculated by equation (17):

$$\therefore \quad N_P = \left(\frac{665\, m^2}{2.75\, m * 8.02\, m} \right) \rightarrow N_P = 30.12 \approx 31$$

∴ The no. of plates is taken as 31.

The separator is having three channels, each one with two packages of plates (Two working + 1 standby)

$$\text{i.e.} \quad Q_A = \left[\frac{300 \left(\dfrac{m^3}{hr} \right)}{3 * 2} \right] \rightarrow Q_A = 50 \frac{m^3}{hr}.$$

Effective separation area: Effective separation area is calculated by making use of Figure 13:

With Kinematic viscosity of 0.00011 *stokes* and plates spacing of around 2 *cm* and with Reynolds number 2000, the flow rate is around 13.1 $\frac{L}{sec}$ so the area from the figure comes out to be around 9 * 10^3 cm^2 = 9000 cm^2 = 9000 * 10^{-4} m^2 = 0.9 m^2.

Total area = 6 * A = 6 * 0.9 m^2 = 5.4 m^2 per pack.

Ancilliary Equipments:

(i) Inlet Pipe

- **Diameter:** 6 *inch* pipe (150 *mm*) minimum
- **Velocity:** We have to use minimum velocity that will avoid suspended solid deposition in the pipe. It should be around $0.6\ \frac{m}{sec}$ for refinery effluent.
- **Diffuser:** Diffusers must be used so as to reduce momentum and to avoid short-circuiting.

(ii) Inlet compartment

- **Dimensions:** Dimensions are the function of flow rate and settleability of the suspended solids. So maximum surface loading rate of around $28.3\ \frac{L}{m^2 * \min}$ must be there.
- **Primary sludge hopper:** Optimum hopper angle of around 55^O (from horizontal). We are not allowed to use slope less than the angle of repose for material removed. Hopper volume is determined by the amount of suspended solids removed and sludge draw off schedule. Provide > 10% of the compartment volume.
- **Primary sludge draw off:** 100 *mm* diameter (minimum) connection with plug valve.
- **Diffuser baffle:** It should be provided so as to distribute the oily wastewater evenly across packed plate inlet.
- **Overflow weir:** Sharp crested vertically adjustable, length as necessary to establish laminar flow velocity to plate pack compartment.

(iii) Coalescing (plate) compartment:

Inclined plates	
Plates type	: Corrugated type
Spacing	: 20 *mm*
Angle	: 45^O
Plate pack orientation	: Down flow
Horizontal plates	
Spacing	: 20 *mm*
Angle	: Zero degrees
Plate pack orientations	: Cross flow with respect to corrugations

(iv) Oil overflow weir: Sharp crested vertically adjustable. If the discharge is directly to outfall sewer, then we have to provide a V - notch for flow measurement.

(v) Secondary sludge draw off:

- **Nozzle:** A 100 *mm* minimum diameter with plug valve.
- **Underflow baffle:** Underflow velocity should not exceed $1.2\ \frac{L}{\text{min}}$.

Some important points to remember which designing the TPI unit

- A TPI Separator is provided with a slotted pipe oil skimmer through which separated oil is routed to slop oil pump. There is valve at the outlet of recovered oil line which is kept closed when the oil is not recovered.
- Oil skimming operation is to be carried out depending on the amount of oil collected on the top of water surface. This is to be done once in a shift.
- Sludge removal lines are to be provided from TPI Bottom to Sludge sump. Water/air connections is to be provided to dechoke the line.
- 1 *foot* space is to be allowed below the plates for sediment storage.
- Add 12 *inches* space minimum head space from the top of the plate pack and the bottom of the vault cover. Then allow 1 *foot* above that for the freeboard.
- Include forebay to collect floatable debris and evenly distribute flow if more than one plate unit is needed. Use a trash track/screen to reduce clogging.
- The sediment - retaining baffle must be upstream of the plate pack at a minimum height of 18 *inches*.

SUMMARY OF TPI SEPARATOR DESIGN

Vertical oil rising velocity	$0.706\ \frac{m}{hr}$.
Calculation of area ❖ **A_P** ❖ **A_{P1}** ❖ **A_A**	 $425\ m^2$ $467.50\ m^2$ $665\ m^2$
Kinematic viscosity	$\upsilon=1.11 * 10^{-6} \frac{m^2}{\text{sec}}$
Length of the separator	$8.02\ m \approx 27$ *feet*
Width of the separator	$2.75\ m \approx 9$ *feet*
Number of plates	31

5.4 DESIGN OF DISSOLVED AIR FLOTATION SYSTEM (DAF SYSTEM)

Unit Design Data	
Influent characteristics:	
Total flow	(300 + 75) m^3/hr (Effluent + Recycled)
Free oil	50 *mg/L*
Emulsified oil	500 *mg/L*
Specific gravity of oil	0.9
Specific gravity of wastewater effluent	1.0
Viscosity of effluent	1.0 *cP*
Temperature (ambient)	25^{O}C
Sulphides	235 *mg/L*
Phenols	100 *mg/L*
Suspended solids	(20 + flocs) *mg/L*
Treated effluent characteristics	
Total oil	< 10 *mg/L*
Suspended solids	< 10 *mg/L*
Sulphides	= 20 *mg/L*
Phenols	= 20 *mg/L*

Equation (18) presents how to calculate the pressure with recycle for DAF system:

From the graph in between $\left(\frac{A}{S}\right)$ ratio and effluent quality (with 10 $\frac{mg}{L}$ as suspended solids), we will get $\left(\frac{A}{S}\right)$ ratio as $0.02\frac{mg}{L}$.

Value of s'_a at ambient temperature 25^{O}C is $16.5\frac{mL}{L}$,

Assumptions:

Fraction of saturation, $f = 0.5$

We will design DAF reactor with an initial concentration of 500 $\frac{mg}{L}$ of emulsified oil.

Here $Q = 300\ \frac{m^3}{hr}$, $Q_R = 75\ \frac{m^3}{hr}$.

By applying all these values in the equation (18), we have:

$$\therefore \quad \frac{A}{S} = \left[\frac{1.3 * 16.5\frac{mL}{L} * (0.5 * P - 1) * 75\frac{m^3}{hr}}{\left(500\frac{mg}{L} * 300\frac{m^3}{hr}\right)}\right]$$

On solving, 0.5 P = 2.8648 ➔ P = 5.7296 *atm*.

Since, $P=\left(\frac{p+101.35}{101.35}\right)$ ➔ 5.7296 ➔ $P=\left(\frac{p+101.35}{101.35}\right)$

∴ p = 479.3 *kPa* ~ 480 *kPa* [acceptable as it is in the range 425 – 620 *kPa*]

Surface area is calculated by the equation (19):

Usually in design of DAF tank, surface loading rate (SLR) is taken in between $0.4-13.4\ \frac{m}{hr}$. In general, we take SLR as $2\ \frac{gpm}{ft^2}$ in case of without recycle condition. If the effluent is recycled we can assume the value of SLR as $1.5-1.6\ \frac{gpm}{ft^2}$.

So, $\text{SLR} = 1.6\ \frac{gpm}{ft^2} = 3.91\left(\frac{m^3}{m^2 * hr}\right) = 3.91\ \frac{m}{hr}$.

∴ $A_r = \left[\frac{300+75\left(\frac{m^3}{hr}\right)}{3.91\left(\frac{m}{hr}\right)}\right]$ ➔ $A_r = 95.87\ m^2 \sim 96\ m^2$.

We are providing two compartments in each DAF tank.

So effective area in each flotation tank = $\left(\frac{96}{2}\right) = 48\ m^2$.

As per consideration, length of tank is not taken more that 40 *feet* [12 *m*, (maximum)] and width of tank is not taken more than 30 *feet* [10 *m*, (maximum)]

With this specification, with the area of 48 m^2, the dimension of tank can be calculated as 10 *m* * 4.8 *m*

$A_R = 48\ m^2 = 10\ m * 4.8\ m$

Detention time is usually taken in between 20 – 30 *minutes*.

Let us assume a detention time of 20 *minutes*.

Thus, volume is calculated by equation (20):

Volume, $V = \left(375\ \frac{m^3}{hr}\right) * \left(\frac{20}{60}\right) hr = 125\ m^3$.

∴ Volume of the DAF tank is obtained as 125 m^3.

Thus, depth of the tank is calculated by equation (21):

∴ Depth of the tank, $d = \left(\frac{125\,m^3}{48\,m^2}\right) \rightarrow d = 2.62\ m \sim 2.7\ m.$

By providing a dashboard of 0.3 m, the depth of the tank, $d = 2.7\ m + 0.3\ m = 3.0\ m$.

∴ Overall dimensions of the tank = 10 m * 4.8 m * 3.0 m

Thus corrected volume, V = 144 m^3.

Corrected volumetric flow rate,

$$Q = 144 * \left(\frac{60}{20}\right) \frac{m^3}{hr} \rightarrow Q = 432 \frac{m^3}{hr}.$$

Equation (22) presents how to calculate solid loading rate:

$$\text{Solid loading rate} = \left[\frac{500\left(\frac{mg}{L}\right) * 10^{-6}\left(\frac{kg}{mg}\right) * 432\left(\frac{m^3}{hr}\right)}{96\ m^2}\right]$$

$$\therefore \quad \text{Solid loading rate} = 2.25\ \frac{kg}{m^2 * hr}$$

Solid loading rate should be in the range in between 1.2 – 3.0$\frac{kg}{m^2 * hr}$. Since solid loading rate obtained is within the range our design is satisfactory.

SUMMARY OF DAF SYSTEM DESIGN

$\left(\frac{A}{S}\right)$ **Ratio**	$0.02\frac{mg}{L}$
Pressure, P	5.7296 *atm*
Gage pressure, p	480 *kPa*
Surface area, A_r	96 m^2
Effective area, A_R	48 m^2
Dimension of the tank (L * B)	10 m * 4.8 m
Detention time, t	20 *min*
Volume of the tank, V	125 m^3
Depth of the tank, d	2.7 m
Depth of the tank including dashboard	3.0 m
Corrected volume	144 m^3
Corrected flow rate	$432\ \frac{m^3}{hr}$
Solid loading rate	$2.25\ \frac{kg}{m^2 * hr}$

5.5 DESIGN OF SEQUENCING BATCH REACTORS (SBR)

Unit Design Data

Wastewater characteristics (Influent characteristics)

Temperature (^{O}C) = 12
Specific gravity = 1.0
Oil (g/m^3) = 20
Total BOD_5 (g/m^3) = 1000
sBOD (g/m^3) = 800
COD (g/m^3) = 1700
sCOD (g/m^3) = 300
rbCOD (g/m^3) = 100
TSS (g/m^3) = 100
VSS (g/m^3) = 40
Phenols (g/m^3) = 100
Sulphides (g/m^3) = 235
Total Kjeldahl Nitrogen (g/m^3) = 115
$NH_4 - N$ (g/m^3) = 74
Total Phosphorus (g/m^3) = 10
bCOD/BOD ratio = 1.6
pH = 7.0 - 8.0

[Note: $\frac{mg}{L} = \frac{g}{m^3}$]

Design conditions and assumptions:

0. Use two tanks.
0. Total depth of liquid when full = 6 m.
0. Decant depth = 30% of the depth of the tank.
0. Sludge Volume Index (SVI) = 150 mL/g.
0. $NO_x \approx 80\%$ of Total Kjeldahl Nitrogen.
0. Use kinetic coefficients from Table 12 and 13.

Step 1: Develop wastewater characteristics needed for process design

G. Determine bCOD using the following equation given under

$bCOD \approx 1.6 * BOD$

$$\rightarrow \quad bCOD = 1.6 * 1000 \frac{g}{m^3} \rightarrow bCOD = 1600 \frac{g}{m^3}$$

$$\therefore \quad bCOD = 1600 \frac{g}{m^3}$$

G. Determine $nbVSS$ concentration with the help of equations (23) and (24), respectively:

$$\rightarrow \quad \frac{bpCOD}{pCOD} = \frac{\left[1.6 * (1000-800)\frac{g}{m^3}\right]}{(1700-300)\frac{g}{m^3}} \rightarrow \frac{bpCOD}{pCOD} = 0.23 \ \&$$

$$(nbVSS) = (1 - 0.23) * 40 \frac{g}{m^3} \ [\text{Since, VSS} = 40 \frac{g}{m^3}]$$

$$(nbVSS) = 30.8 \frac{g}{m^3}$$

G. Calculate $iTSS$ by the equation (25):

$$\therefore \quad iTSS = (100-40) \frac{g}{m^3} = 60 \frac{g}{m^3}$$

Step 2: Determine SBR Operating Cycle

Total cycle time (T_C) consists of fill (t_F), react/aerate (t_A), settle (t_S) and decant (t_D). An idle time (t_I) can also be added. Thus, the total cycle time is given by equation (26):

At least two tanks are required so that when one tank is in the fill period (t_F), the following cycles are occurring in the other tank: aeration (t_A), settling (t_S), and decant (t_D) cycles. Thus, it is shown by equation (27),

$$t_S = t_A + t_S + t_D \qquad \ldots(27)$$

Let us select period times: Assume $t_A = 2$ *hrs*, $t_S = 0.5$ *hrs*, $t_D = 0.5$ *hrs*.

Then, $t_F = (2.0 + 0.5 + 0.5)$ *hrs* = 3.0 *hrs* for each tank (Note: Some aeration may also be done in the fill period)

$$\therefore \quad \text{Total Cycle Time } (T_C) = t_F + (t_A + t_S + t_D) = (3.0 + 3.0)\, hrs = 6.0\, hrs.$$

$$\therefore \quad \text{Number of } \frac{Cycles}{\tan k * day} = \frac{\left[24 \frac{hrs}{day}\right]}{\left[6 \frac{hrs}{Cycle}\right]} = 4 \frac{Cycles}{Tank * day}$$

$$\text{Total number of } \frac{Cycles}{day} = (2\ Tanks) * \left(4\frac{Cycles}{Tank * day}\right) = 8\frac{Cycles}{day}$$

Fill volume per Cycle is calculated from equation (28):

$$\text{Fill volume/cycle} = \frac{\left(7200\,\frac{m^3}{day}\right)}{\left(8\,\frac{Cycles}{day}\right)} = 900\frac{m^3}{Cycle}.$$

Step 3: Determine fill fraction/cycle $\frac{V_F}{V_T}$ allowed and compare to selected design of value of 0.3.

( ) Solve mass balance equation (29) and determine the fill fraction/cycle.

(i) Estimate X_S based on the amount of an assumed sludge volume index (SVI) value of $150\,\frac{mL}{g}$.

Equation (31) presents the formula for sludge volume index (SVI)

Let us assume a SVI of $150\,\frac{mL}{g}$.

$$\therefore \quad \left(150\frac{mL}{g}\right) = \frac{\left[\left(10^3\frac{mL}{L}\right)*\left(10^3\frac{mg}{g}\right)\right]}{X_S} \rightarrow X_S = \frac{\left[\left(10^3\,\frac{mL}{L}\right)*\left(10^3\,\frac{mg}{g}\right)\right]}{\left(150\,\frac{mL}{g}\right)}$$

$$\rightarrow \quad X_S = 6666\,\frac{g}{m^3}.$$

Earlier it is assumed that the reactor mixed liquor suspended solids (MLSS) concentration is $3000\,\frac{g}{m^3}$, i.e. $X = 3000\,\frac{g}{m^3}$

(ii) Determine the Settled Fraction with the help of equation (30):

$$\rightarrow \quad \frac{V_S}{V_T} = \frac{(3000\,\frac{g}{m^3})}{(6666\,\frac{g}{m^3})} \quad \rightarrow \quad \frac{V_S}{V_T} = 0.45$$

Just provide 20% liquid above the sludge blanket so that solids are not removed by decanting mechanism

$$\therefore \quad \frac{V_S}{V_T} = 1.2 * 0.45 = 0.54$$

(iii) Determine the fill fraction by making use of equation (32):

$$\rightarrow \quad \frac{V_F}{V_T} = 1 - 0.54 = 0.46 > 0.3$$

So, $\frac{V_F}{V_T} = 0.3$ is selected.

Step 4: Determine overall hydraulic retention time (HRT, τ)

Full liquid depth = 6 *m*.

Decant depth = 30% of (Full liquid depth) = 0.3 * 6 *m* = 1.8 *m*.

By equation (33), we have:

$$\frac{V_T}{Tank} = \frac{\left(900\frac{m^3}{Tank}\right)}{0.3} \rightarrow \frac{V_T}{Tank} = 3000\frac{m^3}{Tank}$$

Hydraulic retention time is calcluted by equation (34):

$$\text{Overall } \tau = \frac{\left[\left(3000\frac{m^3}{Tank}\right)*\left(2Tanks\right)\right]}{\left(7200\frac{m^3}{day}\right)} \rightarrow \tau = \left(\frac{5}{6}days\right) = \left(\frac{5}{6}\right) * 24\ hrs = 20\ hrs.$$

i. e. Hydraulic retention time (HRT) = 20 *hrs*.

Step 5: Determine Solid Retention Time (SRT)

By making use of equation (35), (36) and (37), equation (38) is obtained and is mentioned here under:

$$\left(P_{X,TSS}\right)*SRT = \frac{Q*Y*\left(S_O - S\right)*SRT}{\left\{1+k_d*\left(SRT\right)\right\}*0.85} + \frac{Q*Y_n*(NO_X)*SRT}{\left[1+(k_{dn})*SRT\right]*0.85} + Q*(nbVSS)*SRT$$

$$+Q*\left(TSS - TSS_O\right)*SRT + \frac{Q*Y*(S_o - S)*(f_d)*(k_d)*SRT^2}{\left[1+(k_d)*SRT\right]*0.85} \quad \ldots(38)$$

As per the equation (39),

$$\left(P_{X,TSS}\right)*SRT = (3000\ m^3) * \left(3000\frac{g}{m^3}\right)$$

$$\therefore \quad \left(P_{X,TSS}\right)*SRT = 9000000\,g.$$

(a) Develop input data to solve the above relationship for SRT:

$nbVSS = 30.8\ \frac{g}{m^3}$ [From step 1(b)]

Assume $S_O \approx S_O - S$. Therefore, So bCOD = 1600 $\frac{g}{m^3}$ [From step 1(a)]

$$Q = \frac{\left(7200\frac{m^3}{day}\right)}{2\ Tanks} \rightarrow Q = 3600\ \frac{m^3}{day * Tank}$$

$iTSS = (100 - 40)\ \frac{g}{m^3} = 60\ \frac{g}{m^3}$ [From step 1(C)]

$NO_X \approx$ 80% of Total Kjeldahl Nitrogen (TKN) → $NO_X = 92\ \frac{g}{m^3}$

Kinetic coefficients are taken from Table 12 and 13, respectively.

$$Y = 0.40\ \frac{g\,VSS}{g\,VSS * bCOD}$$

$$k_D(\text{at } 20^O\text{C}) = 0.12\frac{g\,VSS}{g\,NH_4 - N}$$

By using the equation (40), we obtain:

$$k_D(at\,12^O C) = \left(0.12\ \frac{g\,VSS}{g\,VSS * day}\right) * (1.04)^{12-20} \rightarrow k_D = 0.088\frac{g\,VSS}{g\,VSS * day}$$

$$Y_N = 0.12\ \frac{g\,VSS}{g\,VSS * NH_4 - N}$$

$$k_{DN}(\text{at } 20^O\text{C}) = 0.08\frac{g\,VSS}{g\,VSS * day}$$

Equation (41) is used to obtain k_{DN} at 12^OC.

$$k_{DN}(at\,12^O C) = \left(0.08\ \frac{g\,VSS}{g\,VSS * day}\right) * (1.04)^{12-20} \rightarrow k_{DN} = 0.06\ \frac{g\,VSS}{g\,VSS * day}$$

$$f_D = 0.15\ \frac{g}{g}$$

Substituting all these values in the equation (38), we have:

$$9000000\text{ g} = \frac{\left[\left(3600\,\frac{m^3}{day}\right) * \left(0.40\,\frac{g\ VSS}{g\ VSS * bCOD}\right) * \left(1600\,\frac{g}{m^3}\right) * SRT\right]}{\left[1 + \left(0.088\,\frac{g\ VSS}{g\ VSS * day}\right) * SRT\right] * 0.85}$$

$$+ \left(3600\,\frac{m^3}{day}\right) * \left(30.8\,\frac{g}{m^3}\right) * \text{SRT} + \left(3600\,\frac{m^3}{day}\right) * \left(60\,\frac{g}{m^3}\right) * \text{SRT}$$

$$+ \left[\frac{\left(0.12\,\frac{g\ VSS}{g\,NH_4 - N}\right) * \left(3600\,\frac{m^3}{day}\right) * \left(92\,\frac{g}{m^3}\right) * SRT}{\left\{1 + \left(0.06\,\frac{g\ VSS}{g\ VSS * day}\right) * SRT\right\} * 0.85}\right]$$

$$+ \frac{\left[\left(3600\,\frac{m^3}{day}\right) * \left(0.40\,\frac{g\ VSS}{g\ bCOD}\right) * \left(0.15\,\frac{g}{g}\right) * \left(0.088\,\frac{g\ VSS}{g\ VSS * day}\right) * \left(1600\,\frac{g}{m^3}\right) * (SRT)^2\right]}{\left[1 + \left(0.088\,\frac{g\ VSS}{g\ VSS * day}\right) * (SRT)\right] * 0.85}$$

$$9000000 = \left[\frac{2710588.235 * (SRT) + 35779.765 * (SRT)^2}{1 + 0.088 * (SRT)}\right] + 326880 * (SRT)$$

$$+ \left[\frac{46757.6471 * (SRT)}{1 + 0.06 * (SRT)}\right]$$

With the help of trial and error method, value of SRT ≈ 3.56 *days* (up to two decimal places).

Step 6: Determine MLVSS concentration

Since, we have got the solid retention time SRT as 3.14 *days* [Where, $S_O \approx S_O - S$]

By solving equation (39) and (42); (X_{MLVSS}) is calculated:

$$V_T * X_{MLVSS} = \left[\frac{\left(3600\frac{m^3}{day}\right)*\left(0.40\frac{g\,VSS}{g\,VSS*bCOD}\right)*\left(1600\frac{g}{m^3}\right)*(3.56\ days)}{\left\{1+\left(0.088\frac{g\,VSS}{g\,VSS*day}\right)*(3.56\ days)\right\}}\right]$$

$$+\left[\frac{\left(0.12\frac{g\,VSS}{g\,NH_4-N}\right)*\left(3600\frac{m^3}{day}\right)*\left(92\frac{g}{m^3}\right)*(3.56\ days)}{\left\{1+\left(0.06\frac{g\,VSS}{g\,VSS*day}\right)*(3.56\ days)\right\}}\right]$$

$$+\left(3600\ \frac{m^3}{day}\right)*\left(92\frac{g}{m^3}\right)*(3.56\ days)$$

$$+\frac{\left[\left(3600\frac{m^3}{day}\right)*\left(0.40\frac{g\,VSS}{g\,bCOD}\right)*\left(0.15\frac{g}{g}\right)*\left(0.088\frac{g\,VSS}{g\,VSS*day}\right)*(3.56\,days)^2*\left(1600\frac{g}{m^3}\right)\right]}{\left[1+\left(0.088\frac{g\,VSS}{g\,VSS*day}\right)*(3.56\,days)\right]}$$

$$V_T * X_{MLVSS} = 6968376.892\left(\frac{m^3*g}{m^3}\right) \quad \text{[Since, } V_T = 3000\ m^3\text{]}$$

$$\therefore \quad (X_{MLVSS}) = 2322.79298\frac{g}{m^3} \approx 2322.79\frac{g}{m^3}$$

( ) Determine the fraction of MLVSS

$$\left(\frac{X_{MLVSS}}{X_{MLSS}}\right) = \left(\frac{2322.79298\frac{g}{m^3}}{3000\frac{g}{m^3}}\right) \rightarrow \left(\frac{X_{MLVSS}}{X_{MLSS}}\right) = 0.67365.$$

Step 7: Determine the amount of $NH_4 - N$ oxidized (NO_X)

Equation (43) presents a nitrogen balance from which equation (44) is derived which is mentioned below:

$$(NO_X) = (TKN_O) - (N_E) - 0.12 * \frac{P_{X,BIO}}{Q} \qquad \ldots(44)$$

$\left(P_{X,BIO}\right)$ is obtained by making use of equation (45):

$$\left(P_{X,BIO}\right)=\left[\frac{\left(3600\,\frac{m^3}{day}\right)*\left(0.40\frac{g\,VSS}{g\,VSS*bCOD}\right)*\left(1600\,\frac{g}{m^3}\right)}{\left\{1+\left(0.088\frac{g\,VSS}{g\,VSS*day}\right)*\left(3.56\,days\right)\right\}}\right]$$

$$+\left[\frac{\left(0.12\,\frac{g\,VSS}{g\,NH_4-N}\right)*\left(3600\,\frac{m^3}{day}\right)*\left(92\,\frac{g}{m^3}\right)}{\left\{1+\left(0.06\frac{g\,VSS}{g\,VSS*day}\right)*\left(3.56\,days\right)\right\}}\right]$$

$$+\frac{\left[\left(3600\,\frac{m^3}{day}\right)*\left(0.40\frac{g\,VSS}{g\,bCOD}\right)*\left(0.15\,\frac{g}{g}\right)*\left(0.088\,\frac{g\,VSS}{g\,VSS*day}\right)*\left(1600\frac{g}{m^3}\right)*\left(3.56\,days\right)\right]}{\left[1+\left(0.088\frac{g\,VSS}{g\,VSS*day}\right)*\left(3.56\,days\right)\right]}$$

$$\left(P_{X,BIO}\right)=\ 1838111.716\,\frac{g}{day}\ \rightarrow\ \left(P_{X,BIO}\right)\approx\ 1838.11\,\frac{kg}{day}$$

$$\therefore\left(NO_X\right)=115.00-2.00-\frac{0.12*\left(1838.11\frac{kg}{day}\right)*\left(10^3\,\frac{g}{kg}\right)}{3600\,\frac{m^3}{day}}$$

[Total ammoniacal nitrogen concentration at effluent is $2\frac{mg}{L}$]

$$\therefore\qquad\left(NO_X\right)=\left(115-2-61.27\right)\frac{g}{m^3}\rightarrow\ \left(NO_X\right)=\ 51.73\,\frac{g}{m^3}$$

Step 8: Check degree of nitrification to determine whether NH$_4$ – N will be removed to a level of $2\frac{g}{m^3}$ in a 2 *hour* aeration period.

( ) Determine amount of oxidizable N available:

$NO_X=\ 51.73\,\frac{g}{m^3}=NH_4-N$ in the feed flow that can be oxidized.

$\therefore$ Oxidizable NH_4-N added/cycle:

$$\left(V_F\right)*\left(NO_X\right)=\left(900\,\frac{m^3}{Cycle}\right)*\left(51.73\,\frac{g}{m^3}\right)\ \rightarrow\ \left(V_F\right)*\left(NO_X\right)=\left(46556.64852\frac{g}{Cycle}\right)$$

$NH_4 - N$ remaining before fill = $(V_S)*(N_E)$

$$(N_E) = 2\frac{g}{m^3}\,NH_4 - N$$

∴ $$(V_S)*(N_E) = (V - V_F)*(N_E) = \left\{(3000-900)\frac{m^3}{Tank}\right\}*\left(2\frac{g}{m^3}\right)$$

➔ $$(V_S)*(N_E) = 4200\frac{g}{Tank}$$

∴ Total oxidizable nitrogen (N) at the beginning of cycle

➔ (46556.64852 + 4200) g = 50756.64852 g

∴ Initial concentration is obtained by the equation (46)

➔ $$N_O = \left(\frac{50756.64852}{3000}\frac{g}{m^3}\right) \rightarrow N_O = 16.92\frac{g}{m^3}$$

( ) **Determine react time**

React time is obtained from the equation (47)

(vi) X_N (Nitrifier concentration) is calculated from equation (48)

➔ $$X_N = \left[\frac{\left(0.12\frac{gVSS}{g\,NH_4 - N}\right)*\left(3600\frac{m^3}{day}\right)*\left(92\frac{g}{m^3}\right)*(3.56\ days)}{\left\{1+\left(0.06\frac{gVSS}{gVSS*day}\right)*(3.56\ days)\right\}*\left(3000\ m^3\right)}\right]$$

➔ $$X_N = 39.03887\frac{g}{m^3} \approx 39.04\frac{g}{m^3}$$

$$\mu_{MN}\ (\text{at } 20^{O}\text{C}) = 0.75\frac{g\ VSS}{g\ VSS * day}$$

By making use of equation (49), μ_{MN} at 12^{O}C is calculated:

➔ $$\mu_{MN}\ (\text{at } 12^{O}\text{C}) = \left(0.75\frac{g\ VSS}{g\ VSS * day}\right)*(1.07)^{12-20} \rightarrow \mu_{MN} = 0.44\frac{g\ VSS}{g\ VSS * day}$$

$$K_N\ (\text{at } 20^{O}\text{C}) = \left[\left(0.74\frac{g}{m^3}\right)NH_4 - N\right]$$

Equation (50) is used to obtain K_N at 12^{O}C.

$$K_N(at\,12^{O}C) = \left[\left(0.74\frac{g}{m^3}\right)NH_4 - N\right]*(1.053)^{12-20} \rightarrow K_N = \left[\left(0.49\frac{g}{m^3}\right)NH_4 - N\right]$$

K_O = Half-saturation constant for DO, $\frac{g}{m^3} = 0.5\frac{g}{m^3}$

Dissolved oxygen concentration, $\frac{g}{m^3}$

(vi) Determine the time for reaction

Solve for t for N_O = 16.92 $\frac{g}{m^3}$ and $N_E = 2\ \frac{g}{m^3}$

By making use of equation (47), the time required for reaction is calculated here under:

$$\therefore 0.49\ \ln\left(\frac{16.92}{2}\right)+(16.92-2)=\left(39.04\frac{g}{m^3}\right)*\left[\frac{\left(0.44\frac{g\ VSS}{g\ VSS*day}\right)}{\left(0.12\frac{g\ VSS}{g\ VSS*NH_4-N}\right)}\right]*\left(\frac{2.0}{2.0+0.5}\right)*t$$

➔ $t = 0.13388\ days = 3.21309\ hrs \approx 3.2\ hrs.$

(c) Determine aeration time

Required aeration time = 3.2 *hrs*.

Aeration time selected was 2 *hrs* and therefore aeration is required during part of fill period.

Fill time = 3.0 *hrs*.

Atleast one-half of the fill time should be used for mixing without aeration to provide a selector operation for SVI control.

∴ Total aeration time = $\left(\frac{3.0}{2}+2.0\right)hrs = 3.5\ hrs$

Thus, there is enough sufficient time for nitrification.

Step 9: Determine decant pumping rate

∵ Decant volume = Fill volume and $V_F = 900\frac{m^3}{Fill}$ and Decant time = 0.5 *hrs* = 30 *min*

Decant pumping rate is calculated from equation (51)

$$\therefore \quad \text{Decant pumping rate} = \left(\frac{900\frac{m^3}{Fill}}{30\frac{\min}{Fill}}\right) = 30\ \frac{m^3}{\min}$$

∴ Decant pumping rate = $30\ \frac{m^3}{\min}$

Step 10: Determine oxygen required/tank using equation (52)

$$R_O = \left(3600\ \frac{m^3}{day}\right) * \left(1600\ \frac{g}{m^3}\right) * \left(\frac{1}{10^3}\ \frac{kg}{g}\right) + 4.33 * \left(3600\ \frac{m^3}{day}\right) * \left(92\ \frac{g}{m^3}\right) * \left(\frac{1}{10^3}\ \frac{kg}{g}\right)$$

$$-\ 1.42 * \left(1838.11\ \frac{kg}{day}\right) \rightarrow R_O = 4583.97736\ \frac{kg}{day} \approx 4583.98\ \frac{kg}{day}$$

We have calculated that: $\frac{Aeration\,time}{Cycle} = 3.5\ hrs.$

Number of $\frac{Cycles}{day} = 4$

$\therefore$ Total aeration time $= \left(3.5\frac{hrs}{Cycle}\right) * \left(4\frac{Cycles}{day}\right) = 14\frac{hrs}{day}$

Average oxygen transfer rate is calculated from equation (53):

$$\text{Average oxygen transfer rate} = \left(\frac{4583.98\ \frac{kg}{day}\ of\ O_2}{14\frac{hrs}{day}}\right) = 327.42695\ \frac{kg}{hr} \approx 327.43\ \frac{kg}{hr}$$

[**Note:** Oxygen demand will be higher at beginning of aeration period so that aeration system oxygen transfer capacity must be higher than this oxygen transfer rate. Thus oxygen transfer rate should be multiplied by a factor of 1.5 – 2.0 so as to provide sufficient oxygen transfer at the beginning of cycle and to handle peak load.]

Step 11: Determine sludge production using equation (54)

Sludge production is calculated by making use of equation (39) and equation (54) is derived; where MLSS = X_{TSS}:

$$\left(P_{X,TSS}\right) = \frac{\left(3000\ \frac{m^3}{Tank}\right) * (2\,Tanks) * \left(3000\ \frac{g}{m^3}\right) * \left(10^{-3}\ \frac{kg}{g}\right)}{3.56\ days} = 5898.87640\ \frac{kg}{day}$$

$$\text{bCOD removed} = \left(7200\frac{m^3}{day}\right) * \left(1600\frac{g}{m^3}\right) * \left(10^{-3}\frac{kg}{g}\right) = 11520\ \frac{kg\,bCOD}{day}$$

$$\text{BOD removed} = \frac{\left(11520\frac{kg}{day}\right)}{\left(1.6\ \frac{kg\,bCOD}{kg\,BOD}\right)} = 7200\frac{kg\,BOD}{day}$$

Observed yield, $\frac{g\,TSS}{g\,BOD}$ [equation (55)] $= \left(\frac{5898.87640\,\frac{kg}{day}}{7200\,\frac{kg\,BOD}{day}} \right) = 0.82\frac{g\,TSS}{g\,BOD}$

Observed yield, $\frac{g\,VSS}{g\,BOD}$ [equation (56)] $= \left(0.82\frac{g\,TSS}{g\,BOD} \right) * \left(0.67\frac{g\,VSS}{g\,TSS} \right) = 0.54\,\frac{g\,VSS}{g\,BOD}$

Observed yield, $\frac{g\,TSS}{g\,bCOD}$ [equation (57)] $= \left(\frac{5898.87640\,\frac{kg}{day}}{11520\,\frac{kg}{day}} \right) = 0.51\,\frac{g\,TSS}{g\,bCOD}$

Step 12: Determine $\left(\frac{F}{M}\right)$ ratio and BOD volumetric loading

(a) $\left(\frac{F}{M}\right)$ Ratio is calculated from equation (58):

$$\left(\frac{F}{M}\right) \text{Ratio} = \left[\frac{\left(3600\,\frac{m^3}{day}\right) * \left(1000\,\frac{g}{m^3}\right)}{\left(2322.79\,\frac{g}{m^3}\right) * \left(3000\,m^3\right)} \right] \rightarrow \left(\frac{F}{M}\right) = 0.52\,\frac{g}{g * day}$$

(b) BOD volumetric loading is obtained from equation (59):

$$L_{ORG} = \frac{kg\,BOD}{m^3 * day} = \left(\frac{Q * S_O}{V}\right) = \left[\frac{\left(7200\frac{m^3}{day}\right) * \left(1000\frac{g}{m^3}\right)}{\left(10^3\,\frac{kg}{g}\right) * \left(3000\,m^3\right)} \right]$$

$$\therefore \quad L_{ORG} = 2.4\frac{kg}{m^3 * day}$$

In case of SBR unit, $\left(\frac{F}{M}\right)$ ratio is coming as 0.51. Since the value of $\left(\frac{F}{M}\right)$ ratio ranges in between 0.15 - 0.6 in case of industrial wastewater and the value is within this range. So, the design is satisfactory.

Step 13: Prepare design summary for average conditions

Design parameter	***Unit***	**Value**
Average flow	*m^3/day*	7200
Average BOD load	*kg/day*	7200
Average TKN load	*kg/day*	1838.11
Number of tanks	*Number*	2
React time	*hours*	2
Fill time	*hours*	2
Total aeration time	*hours*	3.5
Settle time	*hours*	0.5
Decant time	*hours*	0.5
Cycle time	*hours*	6
Total SRT	*day*	3.56
Tank volume	*m^3/Tank*	3000
Fill volume/cycle	*m^3/Cycle*	900
Fill volume/Tank volume	*Ratio*	0.3
Decant depth	*m*	1.8
Tank depth	*m*	6
MLSS	*g/m^3*	3000
MLVSS	*g/m^3*	2322.79
(F/M) ratio	*g/(g*day)*	0.52
Volumetric BOD load	*kg/(m^3 * day)*	2.4
Decant pumping rate	*m^3/min*	30
Sludge production	*kg/day*	5898.88
Observed yield	*kg VSS/kg BOD* *kg TSS/kg bCOD*	0.54 0.51
Average oxygen required/tank	*kg/day*	4583.98
Total aeration time/(day*tank)	*hours*	14
Average oxygen transfer rate	*kg/hr*	327.43
Overall Volume	*m^3*	3600
Tank area	*m * m*	24.5 *24.5
No: of Blowers	*Number*	3
Blower power	*hP*	60

STUDY OF VARIATION OF DIFFERENT PARAMETERS WITH THE CHANGE OF TEMPERATURE

Solid retention time (SRT):

Solid retention time can be calculated by 2 methods:

(0) Trial and error method

(0) By using polynomial equation.

Here we are using the second method as trial and error method is cumbersome.

By inserting all the values in equation (38), except for k_d and k_{dn} as temperature is being changed. Thus we will get the equation as:

$$9000000 = \left[\frac{2710588.235*(SRT)+35779.765*(SRT)^2}{1+k_d*(SRT)}\right] + 326880 * (SRT) + \left[\frac{46757.6471 * (SRT)}{1+0.06 * (SRT)}\right]$$

$$1 = \left[\frac{0.30118*(SRT)+0.00398 * (SRT)^2}{1+k_d * (SRT)}\right] + 0.03632 * (SRT) + \left[\frac{0.00520 * (SRT)}{1+k_{dn} * (SRT)}\right]$$

$$\begin{aligned}&\left\{0.30118*(SRT)+0.00398*(SRT)^2\right\}*\left\{1+k_{dn}*(SRT)\right\}\\ &\quad + 0.03632*(SRT)*\left\{1+k_{dn}*(SRT)\right\}*\left\{1+k_d*(SRT)\right\}\\ &\quad + 0.00520*\left\{1+k_d*(SRT)\right\} - \left\{1+k_{dn}*(SRT)\right\}*\left\{1+k_d*(SRT)\right\} = 0\end{aligned}$$

On solving and rearranging the common terms, the above equation can be converted into:

$$\begin{aligned}&(0.00398 * k_{dn} + 0.03632*k_d*k_{dn})*(SRT)^3\\ &\quad + (0.3375 * k_{dn} + 0.04152 * k_d - k_d * k_{dn} + 0.00398)*(SRT)^2\\ &\quad + (0.3427 - k_d - k_{dn}) * (SRT) - 1.000 = 0\end{aligned}$$

$$A*(SRT)^3 + B*(SRT)^2 + C*(SRT) + D = 0$$

Where,

$A=(0.00398+0.03632*k_d*k_{dn})$; $B=(0.3375 * k_{dn} + 0.04152 * k_d - k_d * k_{dn} + 0.00398)$

$C=(0.3427 - k_d - k_{dn})$; $D=-1.0000$

Only one positive root obtained here is mentioned in the Table given below:

Table 15: Formation of Equations for the calculation of SRT

Temperature	k_d	k_{dn}	A	B	C	D	SRT
10	0.08107	0.05405	0.000374229	0.021204849	0.207587166	- 1.0000	3.49
11	0.08431	0.05621	0.000395818	0.02171158	0.202182653	- 1.0000	3.52
12	0.08768	0.05846	0.000418811	0.022223708	0.196561959	- 1.0000	3.56
13	0.09119	0.06079	0.000443307	0.022740235	0.190716437	- 1.0000	3.59
14	0.09484	0.06323	0.000469416	0.023260024	0.184637095	- 1.0000	3.63
15	0.09863	0.06575	0.000497252	0.023781785	0.178314579	- 1.0000	3.67
16	0.10258	0.06838	0.000526941	0.024304064	0.171739162	- 1.0000	3.71
17	0.10670	0.07112	0.000558617	0.024825218	0.164900728	- 1.0000	3.76
18	0.11095	0.07396	0.000592425	0.025343406	0.157788757	- 1.0000	3.81
19	0.11538	0.07692	0.000628521	0.025856568	0.150392308	- 1.0000	3.85
20	0.12	0.08	0.000667072	0.0263624	0.1427	- 1.0000	3.91
21	0.1248	0.032	0.00070826	0.026858336	0.1347	- 1.0000	3.96
22	0.12979	0.08653	0.000752278	0.027341522	0.12638	- 1.0000	1.02
23	0.13498	0.08999	0.000799338	0.027808788	0.1177272	- 1.0000	4.09
24	0.14038	0.09359	0.000849665	0.028256622	0.108728288	- 1.0000	4.15
25	0.14600	0.09733	0.000903502	0.028681135	0.09936942	- 1.0000	4.23
26	0.15184	0.10123	0.000961113	0.02907803	0.089636196	- 1.0000	4.30
27	0.15791	0.10527	0.00102278	0.029442563	0.079513644	- 1.0000	4.38
28	0.16423	0.10949	0.001088809	0.029769503	0.06898619	- 1.0000	4.47
29	0.17080	0.11386	0.001159528	0.030053089	0.058037638	- 1.0000	4.56
30	0.17763	0.11842	0.001235293	0.030286983	0.046651143	- 1.0000	4.66

Table 16: Variation of Different Parameters with the Change of Temperature

Temperature, ^0C	10	11	12	13	14	15	16	17	18	19	20
Average flow, m^3/day	7200	7200	7200	7200	7200	7200	7200	7200	7200	7200	7200
Average BOD load, *kg/day*	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Temperature, ^0C	10	11	12	13	14	15	16	17	18	19	20
No: of tanks	2	2	2	2	2	2	2	2	2	2	2
Fill time, *hr*	3	3	3	3	3	3	3	3	3	3	3
React time, *hr*	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Total aeration time, *hr*	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Total SRT, *days*	3.49	3.52	3.56	3.59	3.63	3.67	3.71	3.76	3.81	3.85	3.91
Total volume, m^3	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000
Fill volume/cycle, $m^3/Cycle$	900	900	900	900	900	900	900	900	900	900	900
Fill volume/tank volume	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
MLSS, g/m^3	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000
MLVSS, g/m^3	2317.30	2317.79	2322.79	2321.56	2324.63	2326.69	2327.72	2332.58	2336.21	2333.97	2339.80
F/M, *g/(g*day)*	0.51784	0.51773	0.51662	0.51689	0.51621	0.51575	0.51552	0.51445	0.51365	0.51415	0.51286
BOD volumetric loading, $kg/(m^3 * day)$	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Sludge production, *kg/day*	6017.20	5965.91	5898.88	5849.58	5785.12	5722.07	5660.38	5585.11	5511.81	5454.55	5370.84
Observed yield, *g TSS/g BOD*	0.84357	0.82860	0.81929	0.81244	0.80349	0.79473	0.78617	0.77571	0.76553	0.75758	0.74595
Observed yield, *g VSS/g BOD*	0.55332	0.54872	0.54372	0.53889	0.53366	0.52831	0.52285	0.51697	0.51098	0.50519	0.49868
Observed yield, *g TSS/g bCOD*	0.52233	0.51787	0.51206	0.50778	0.50218	0.49671	0.49135	0.48482	0.47846	0.47348	0.46622
Average oxygen required, *kg/day*	4535.70	4558.84	4583.98	4608.28	4634.60	4661.51	4688.99	4718.55	4748.67	4777.80	4810.53
Average oxygen transfer rate, *kg/hr*	323.98	325.63	327.43	329.16	331.04	332.97	334.93	337.04	339.19	341.27	343.61

Table: Variation of Different Parameters with the Change of Temperature (Contd.)

Temperature, ^0C	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**	**29**	**30**
Average flow, m^3/day	7200	7200	7200	7200	7200	7200	7200	7200	7200	7200
Average BOD load, *kg/day*	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Temperature, ^0C	21	22	23	24	25	26	27	28	29	30
No: of tanks	2	2	2	2	2	2	2	2	2	2
Fill time, *hr*	3	3	3	3	3	3	3	3	3	3
React time, *hr*	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Total aeration time, *hr*	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Total SRT, *days*	3.96	4.02	4.09	4.15	4.23	4.30	4.38	4.47	4.56	4.66
Total volume, m^3	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000
Fill volume/cycle, $m^3/Cycle$	900	900	900	900	900	900	900	900	900	900
Fill volume/tank volume	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
MLSS, g/m^3	3000	3000	3000	3000	3000	3000	3000	3000	3000	3000
MLVSS, g/m^3	2339.77	2342.88	2348.80	2349.03	2355.91	2357.14	2360.65	2366.17	2369.84	2375.19
F/M, *g/(g*day)*	0.51287	0.51219	0.51089	0.51085	0.50936	0.50909	0.50833	0.50715	0.50636	0.50522
BOD volumetric loading, $kg/(m^3 * day)$	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
Sludge production, *kg/day*	5303.03	5223.88	5134.47	5060.24	4964.54	4883.72	4794.52	4697.99	4605.26	4506.44
Observed yield, *g TSS/g BOD*	0.73653	0.72554	0.71312	0.70281	0.68952	0.67829	0.66591	0.65250	0.63962	0.62589
Observed yield, *g VSS/g BOD*	0.49238	0.48567	0.47857	0.47169	0.46413	0.45681	0.44913	0.44112	0.43308	0.42475
Observed yield, *g TSS/g bCOD*	0.46033	0.45346	0.44570	0.43926	0.43095	0.42393	0.41619	0.40781	0.39976	0.39118
Average oxygen required, *kg/day*	4842.21	4875.91	4911.60	4946.14	4984.15	5020.89	5059.43	5099.67	5140.00	5181.84
Average oxygen transfer rate, *kg/hr*	345.87	348.28	350.83	353.30	356.01	358.64	361.39	364.26	367.14	370.13

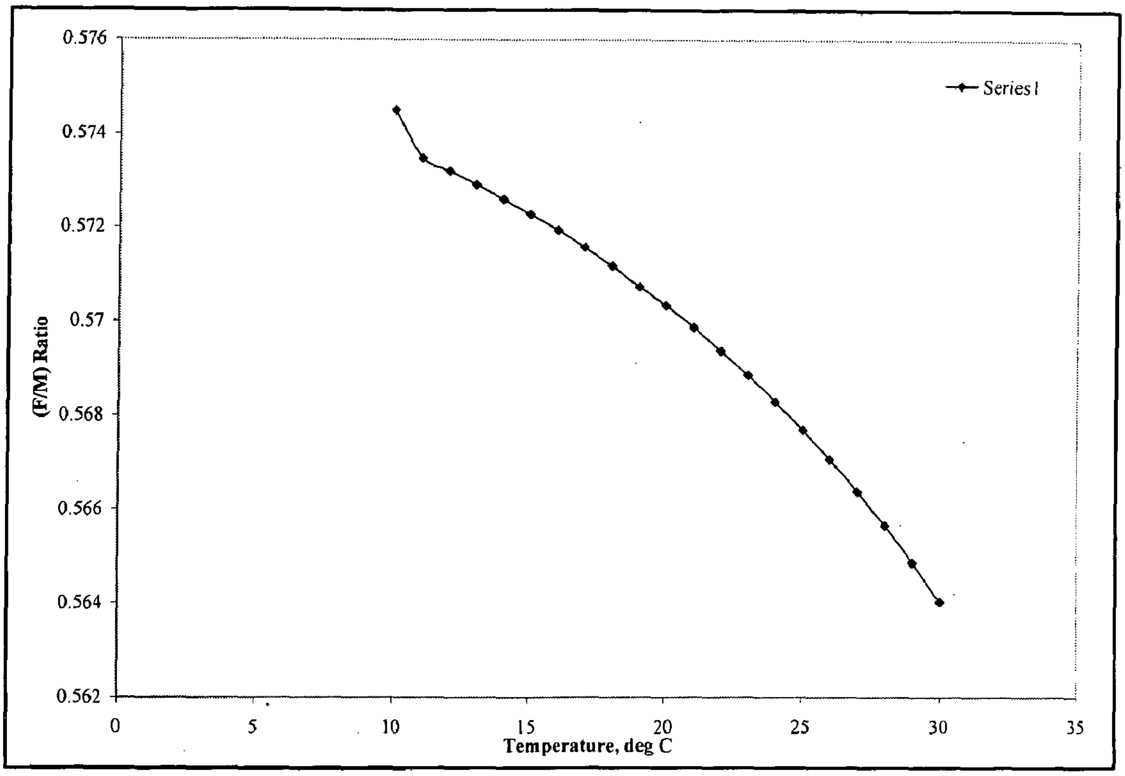


Figure 15: Plot in between Temperature and (F/M) Ratio.

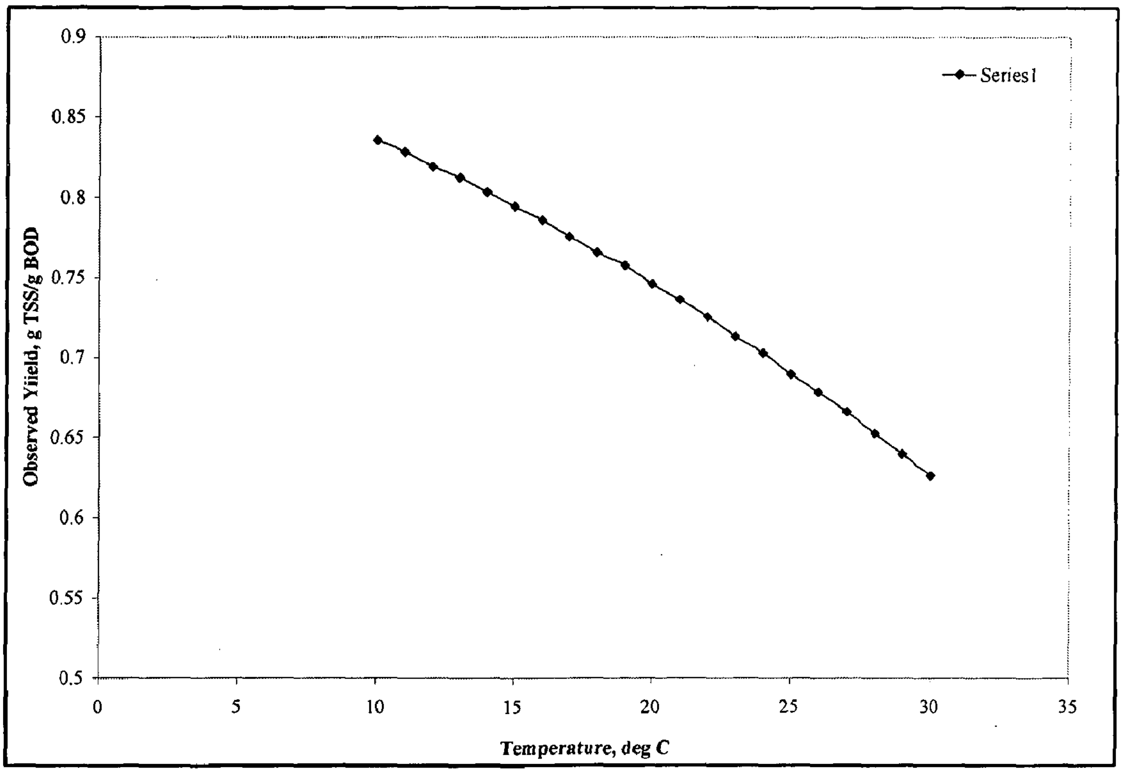


Figure 16: Plot in between Temperature and Observed Yield, g TSS/g BOD.

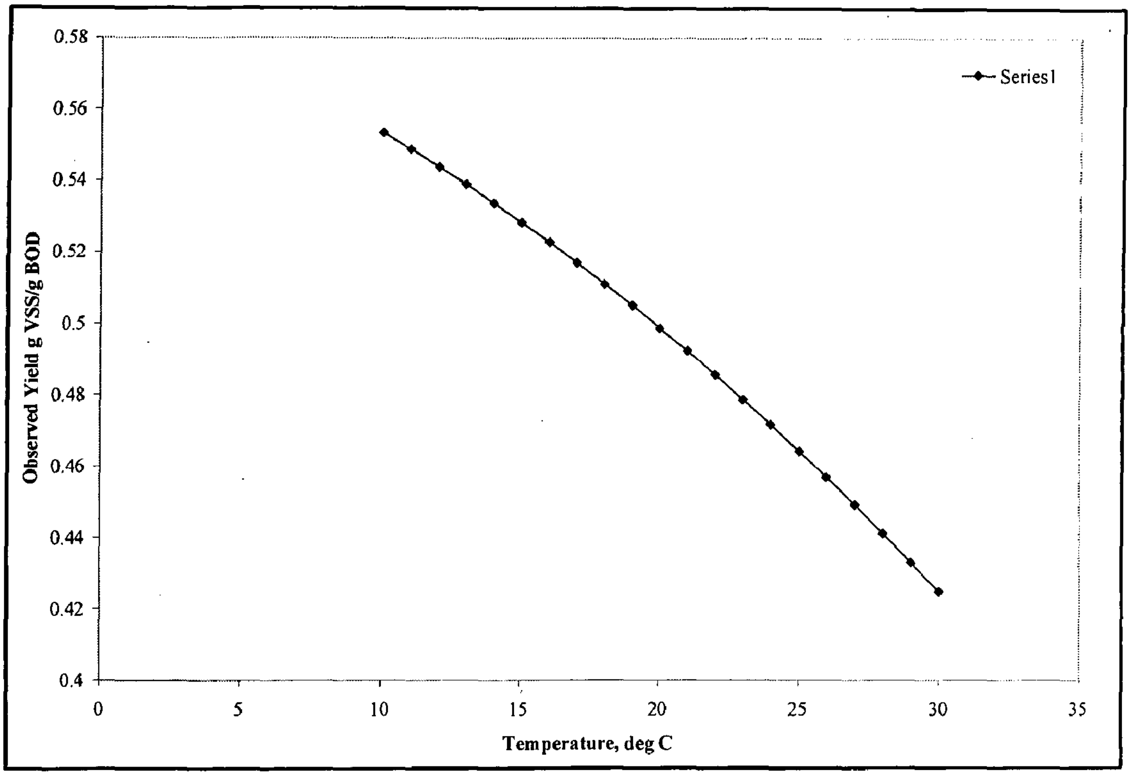


Figure 17: Plot in between Temperature and Observed Yield, g VSS/g BOD.

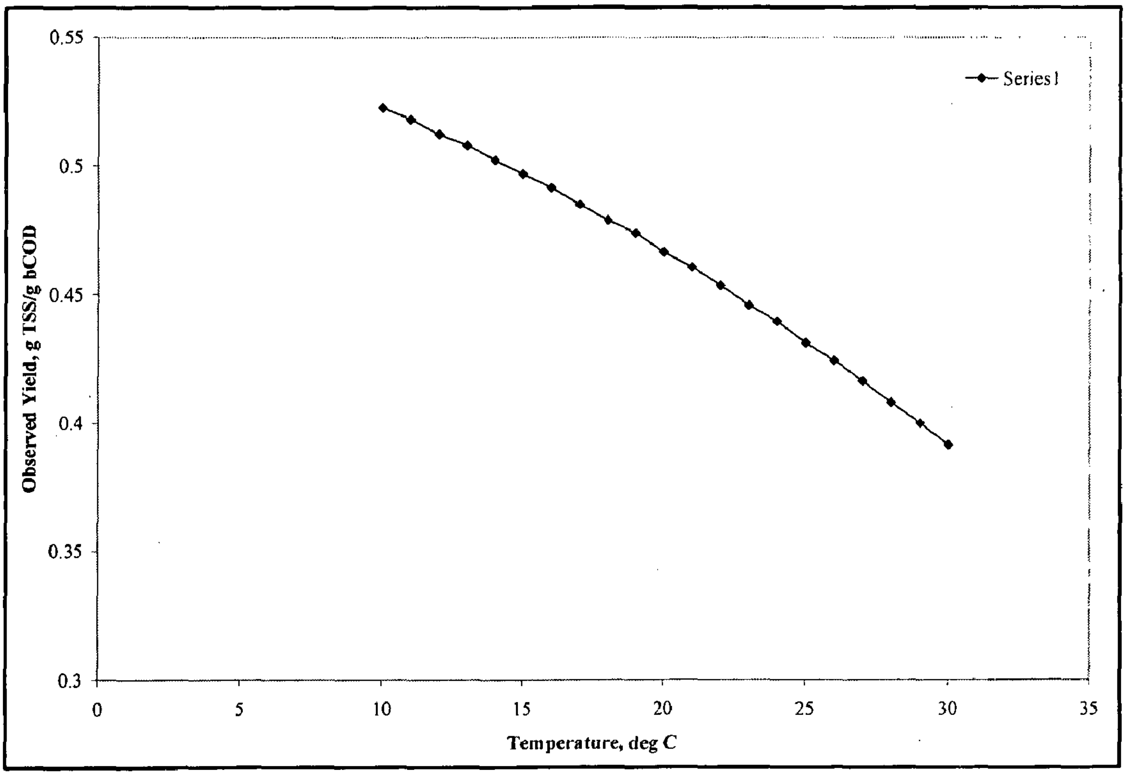


Figure 18: Plot in between Temperature and Observed Yield, g TSS/g bCOD.

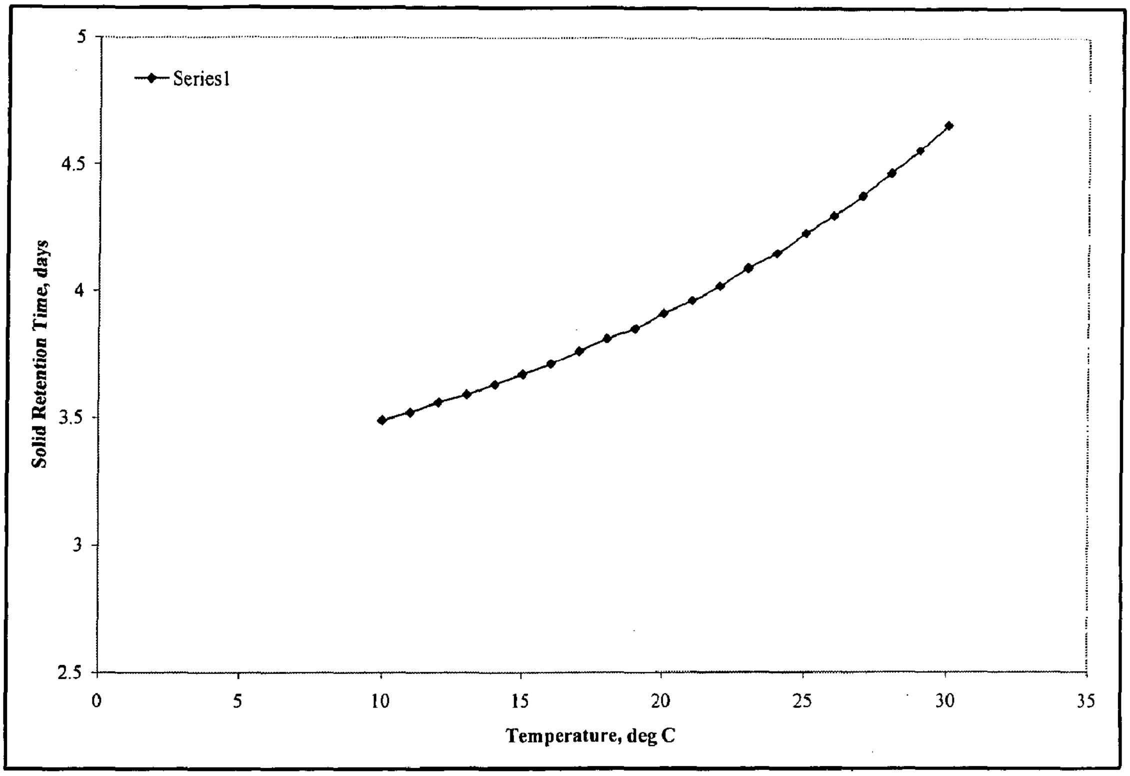


Figure 19: Plot in between Temperature and Solid Retention Time (SRT).

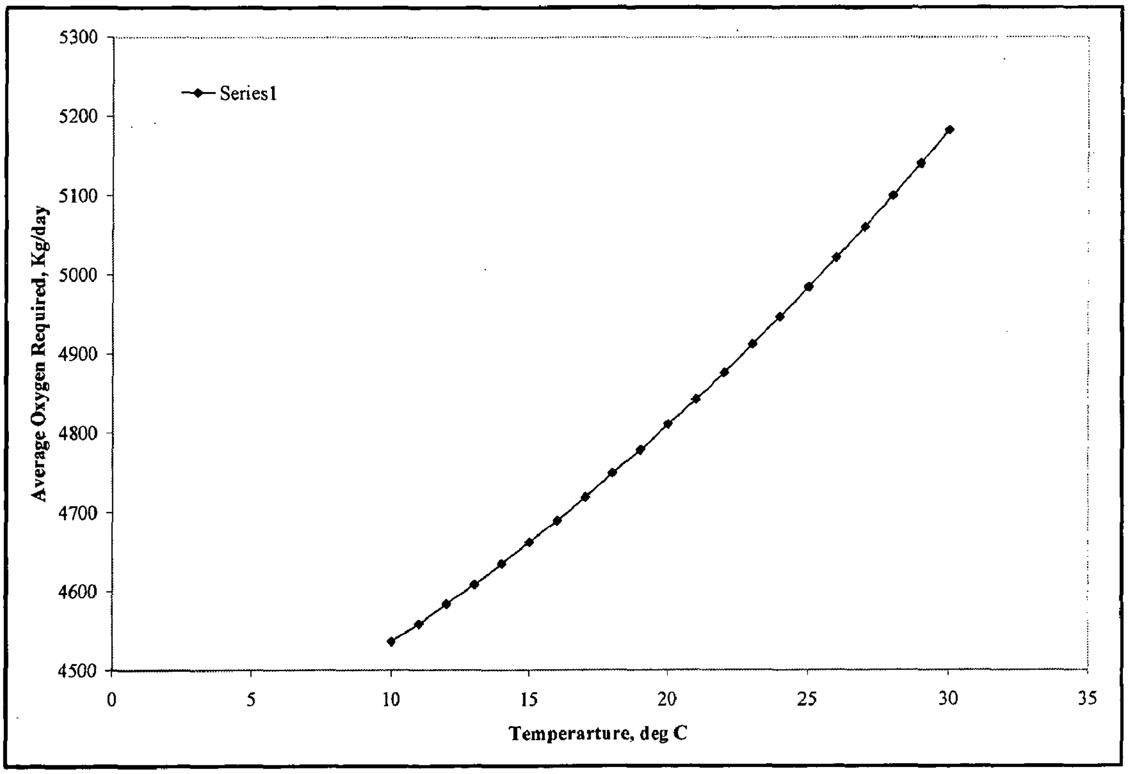


Figure 20: Plot in between Temperature and Average Oxygen Required.

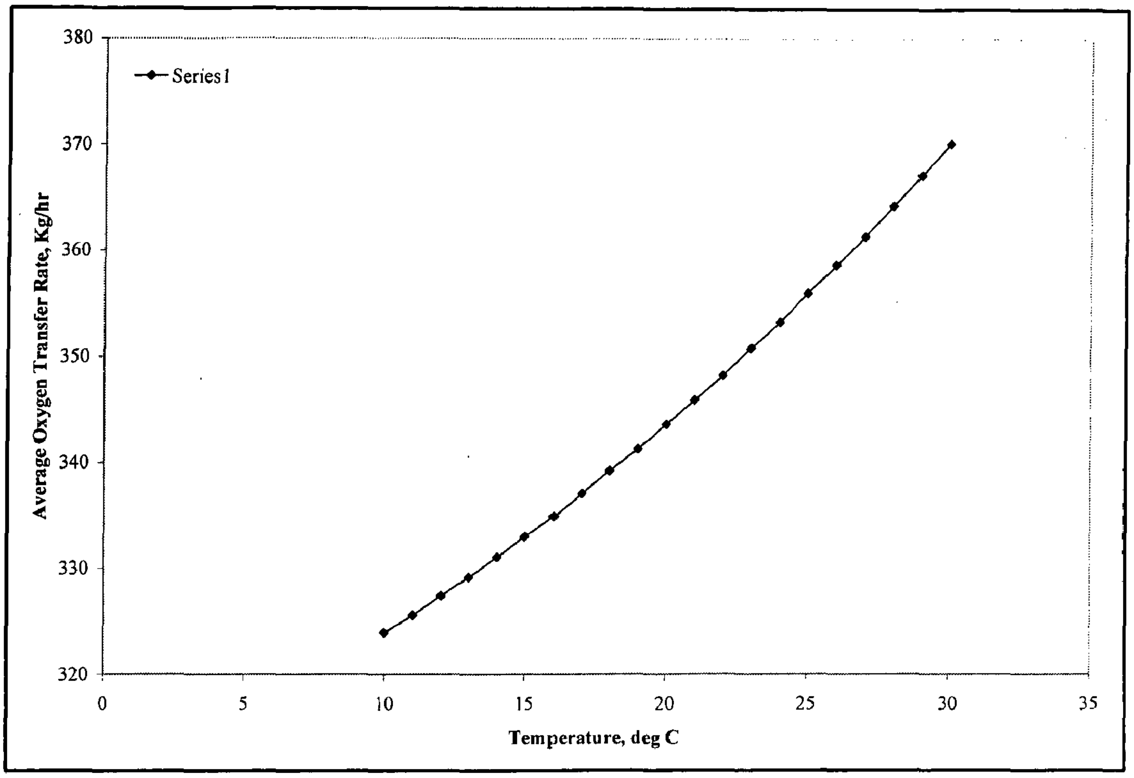


Figure 21: Plot in between Temperature and Average Oxygen Transfer Rate (AOUTR).

6.5 DESIGN OF MEMBRANE BIOREACTORS (MBR)

Unit Design Data	
Wastewater characteristics (Influent characteristics)	
Temperature (^{O}C)	= 25
Specific gravity	= 1.0
Oil (g/m^3)	= 20
Total BOD_5 (g/m^3)	= 100
sBOD (g/m^3)	= 80
COD (g/m^3)	= 200
sCOD (g/m^3)	= 30
rbCOD (g/m^3)	= 25
TSS (g/m^3)	= 20
VSS (g/m^3)	= 5
Phenols (g/m^3)	= 50
Sulphides (g/m^3)	= 40
Total Kjeldahl Nitrogen (g/m^3)	= 30
$NH_4 - N$ (g/m^3)	= 20
Total Phosphorus (g/m^3)	= 7.0
bCOD/BOD ratio	= 1.6
pH	= 7. 0 – 8.0

[Note: $\frac{mg}{L} = \frac{g}{m^3}$]

Design conditions and assumptions:

0. Use two tanks.
0. Sludge Volume Index (SVI) = $150 \frac{mL}{g}$.
0. $NO_X \approx 95\%$ of Total Kjeldahl Nitrogen.
0. Use kinetic coefficients from Table 12 and 13.

Step 1: Develop wastewater characteristics needed for process design

- Determine bCOD using the following equation given under

$$\text{bCOD} \approx 1.6 * \text{BOD}$$

$$\text{bCOD} = 1.6 * 100\,\frac{g}{m^3} \rightarrow \text{bCOD} = 160\,\frac{g}{m^3}$$

$$\therefore \quad \text{bCOD} = 160\,\frac{g}{m^3}$$

- Determine $nbVSS$ concentration with the help of equations (23) and (24), respectively:

$$\frac{bpCOD}{pCOD} = \frac{\left[1.6*(100-80)\frac{g}{m^3}\right]}{(200-30)\frac{g}{m^3}} \rightarrow \frac{bpCOD}{pCOD} = 0.19\ \&$$

$$(nbVSS) = (1-0.19) * 5\,\frac{g}{m^3}\ \left[\text{Since, VSS} = 5\,\frac{g}{m^3}\right]$$

$$\therefore \quad (nbVSS) = 4.059\,\frac{g}{m^3}$$

- Calculate $iTSS$ by the equation (25):

$$iTSS = (20-5)\,\frac{g}{m^3} = 15\,\frac{g}{m^3}$$

Step 2: Determine MBR Operating Cycle

Let's take a cycle time of 1.2 hours for 1 complete cycle and take an aeration time of 20 minutes. The total cycle time is given by:

$$\therefore \quad \text{Number of } \frac{Cycles}{Tank * day} = \frac{\left[24\,\frac{hrs}{day}\right]}{\left[1.2\,\frac{hrs}{Cycle}\right]} = 20\,\frac{Cycles}{Tank * day}$$

$$\text{Total number of } \frac{Cycles}{day} = (2\ Tanks) * 20\,\frac{Cycles}{Tank * day} = 40\,\frac{Cycles}{day}$$

$$\text{Fill volume/cycle} = \frac{\left(7200\,\frac{m^3}{day}\right)}{\left(40\,\frac{Cycles}{day}\right)} = 180\,\frac{m^3}{Cycle}.$$

Step 3: Assume fill fraction

A fill fraction value of 0.3 is selected (i.e. $\frac{V_F}{V_T}$ = 0.3) [The recommended value is 0.3.]

Step 4: Determine overall hydraulic retention time (HRT, τ)

By equation (33), we have:

$$\therefore \quad \frac{V_T}{Tank} = \frac{\left(180\,\frac{m^3}{Tank}\right)}{0.3} \rightarrow \frac{V_T}{Tank} = 600\,\frac{m^3}{Tank}$$

Hydraulic retention time (HRT) is calcluted by equation (34):

$$\text{Overall } \tau = \frac{\left[\left(600\,\frac{m^3}{Tank}\right)*(2\,Tanks)\right]}{\left(7200\,\frac{m^3}{day}\right)} \rightarrow \tau = \left(\frac{4}{24}days\right) = \left(\frac{4}{24}days\right) * 24\,hrs = 4\,hrs.$$

∴ Hydraulic retention time (HRT) = 4 *hrs.*

Hydraulic retention time should range in between 4 – 6 *hours*. Since τ is coming as 4 hrs. So it's coming within the range.

Step 5: Determine Solid Retention Time (SRT)

By making use of equation (35), (36) and (37), equation (38) is obtained and is mentioned here under:

$$\left(P_{X,TSS}\right)*SRT = \frac{Q*Y*\left(S_O-S\right)*SRT}{\left\{1+k_d*\left(SRT\right)\right\}*0.85} + \frac{Q*Y_n*(NO_X)*SRT}{\left[1+(k_{dn})*SRT\right]*0.85} + Q*(nbVSS)*SRT$$

$$+Q*\left(TSS-TSS_O\right)*SRT + \frac{Q*Y*(S_o-S)*(f_d)*(k_d)*SRT^2}{\left[1+(k_d)*SRT\right]*0.85} \quad \ldots(38)$$

As per the equation (39),

$$\left(P_{X,TSS}\right)*SRT = (600\,m^3)*\left(5000\,\frac{g}{m^3}\right)$$

$$\therefore \quad \left(P_{X,TSS}\right)*SRT = 3000000\,g.$$

(a) Develop input data to solve the above relationship for SRT:

$nbVSS = 4.059\ \frac{g}{m^3}$ [From step 1(b)]

Assume $S_O \approx S_O - S$. Therefore, $S_O - S \approx bCOD = 160\ \frac{g}{m^3}$ [From step 1(a)]

$$Q = \frac{\left(7200\ \frac{m^3}{day}\right)}{2\ Tanks} \rightarrow Q = 3600\ \frac{m^3}{day * Tank}$$

$iTSS = (20 - 5)\ \frac{g}{m^3} = 15\ \frac{g}{m^3}$ [From step 1(C)]

$NO_X \approx 95\%$ of Total Kjeldahl Nitrogen (TKN) → $NO_X = 28.5\ \frac{g}{m^3}$

Kinetic coefficients are taken from Table 12 and 13, respectively.

$$Y = 0.40\ \frac{g\,VSS}{g\,VSS * bCOD}$$

$$k_D(\text{at } 20^oC) = 0.12\ \frac{gVSS}{g\,NH_4 - N}$$

By using the equation (40), we obtain:

$$k_D(at\,25^o C) = \left(0.12\frac{gVSS}{gVSS * day}\right) * (1.04)^{25-20} \rightarrow K_D = 0.146\ \frac{gVSS}{gVSS * day}$$

$$Y_N = 0.12\frac{g\ VSS}{g\ VSS * NH_4 - N}$$

$$k_{DN}(\text{at } 20^oC) = 0.08\frac{gVSS}{gVSS * day}$$

Equation (41) is used to obtain k_{DN} at 25^oC.

$$k_{DN}(at\,25^o C) = \left(0.08\frac{gVSS}{gVSS * day}\right) * (1.04)^{25-20} \rightarrow K_{DN} = 0.097\ \frac{gVSS}{gVSS * day}$$

$$f_D = 0.15\ \frac{g}{g}$$

Substituting all these values in the equation (38), we have:

$$3000000\ g=\frac{\left[\left(3600\ \frac{m^3}{day}\right)*\left(0.40\ \frac{g\,VSS}{g\,VSS\ *\ bCOD}\right)*\left(160\ \frac{g}{m^3}\right)*\ SRT\right]}{\left[1+\left(0.146\ \frac{g\,VSS}{g\,VSS\ *\ day}\right)*\ SRT\right]*\ 0.85}$$

$$+\left(3600\ \frac{m^3}{day}\right)*\left(4.059\ \frac{g}{m^3}\right)*\ \mathrm{SRT}+\left(3600\ \frac{m^3}{day}\right)*\left(15\frac{g}{m^3}\right)*\ \mathrm{SRT}$$

$$+\left[\frac{\left(0.12\ \frac{g\,VSS}{g\,NH_4-N}\right)*\left(3600\ \frac{m^3}{day}\right)*\left(28.5\ \frac{g}{m^3}\right)*\ SRT}{\left\{1+\left(0.097\ \frac{g\,VSS}{g\,VSS\,*\,day}\right)*SRT\right\}*\ 0.85}\right]$$

$$+\frac{\left[\left(3600\ \frac{m^3}{day}\right)*\left(0.40\ \frac{g\,VSS}{g\ bCOD}\right)*\left(0.15\frac{g}{g}\right)*\left(0.146\ \frac{g\ VSS}{g\ VSS\ *\ day}\right)*\left(160\frac{g}{m^3}\right)*(SRT)^2\right]}{\left[1+\left(0.146\frac{g\ VSS}{g\ VSS\ *\ day}\right)*(SRT)\right]*\ 0.85}$$

$$3000000=\left[\frac{271058.8235\ *(SRT)+5936.1883\ *(SRT)^2}{1+0.146\ *\ (SRT)}\right]+68612.4\ *\ (\mathrm{SRT})$$

$$+\left[\frac{14484.7059\ *\ (SRT)}{1+0.097\ *\ (SRT)}\right]$$

With the help of trial and error method, value of SRT = 16.424 ≈ 16.4 *days* (up to two decimal places).

Step 6: Determine MLVSS concentration

Since, we have got the solid retention time SRT = 16.4 *days* [Where, $S_O \approx S_O - S$]

By solving equation (39) and (42); (X_{MLVSS}) is calculated:

$$V_T * X_{MLVSS} = \left[\frac{\left(3600 \frac{m^3}{day}\right) * \left(0.40 \frac{gVSS}{gVSS*bCOD}\right) * \left(160 \frac{g}{m^3}\right) * (16.4\ days)}{\left\{1 + \left(0.146 \frac{gVSS}{gVSS*day}\right) * (16.4\ days)\right\}} \right]$$

$$+ \left[\frac{\left(0.12 \frac{gVSS}{g\,NH_4 - N}\right) * \left(3600 \frac{m^3}{day}\right) * \left(28.5 \frac{g}{m^3}\right) * (16.4\ days)}{\left\{1 + \left(0.097 \frac{g\,VSS}{g\,VSS\,*day}\right) * (16.4\ days)\right\}} \right]$$

$$+ \left(3600 \frac{m^3}{day}\right) * \left(4.059 \frac{g}{m^3}\right) * (16.4\ days)$$

$$+ \frac{\left[\left(3600 \frac{m^3}{day}\right) * \left(0.40 \frac{g\,VSS}{g\,bCOD}\right) * \left(0.15 \frac{g}{g}\right) * \left(0.146 \frac{g\,VSS}{g\,VSS * day}\right) * (16.4\ days)^2 * \left(160 \frac{g}{m^3}\right)\right]}{\left[1 + \left(0.146 \frac{gVSS}{gVSS * day}\right) * (16.4\ days)\right]}$$

$$V_T * X_{MLVSS} = 1830561.886 \left(\frac{m^3 * g}{m^3}\right) \quad [\text{Since, } V_T = 600\ m^3]$$

$$\therefore \quad (X_{MLVSS}) \approx 3050.936477 \frac{g}{m^3}$$

( ) Determine the fraction of MLVSS

$$\left(\frac{X_{MLVSS}}{X_{MLSS}}\right) = \left(\frac{3050.936477 \frac{g}{m^3}}{5000 \frac{g}{m^3}}\right) \rightarrow \left(\frac{X_{MLVSS}}{X_{MLSS}}\right) = 0.61019$$

Step 7: Determine the amount of $NH_4 - N$ oxidized (NO_X)

Equation (43) presents a nitrogen balance from which equation (44) is derived which is mentioned below:

$$(NO_X) = (TKN_O) - (N_E) - 0.12 * \frac{P_{X,BIO}}{Q} \qquad \ldots(44)$$

$(P_{X,BIO})$ is obtained by making use of equation (45):

$$\left(P_{X,BIO}\right)=\left[\frac{\left(3600\,\frac{m^3}{day}\right)*\left(0.40\,\frac{g\,VSS}{g\,VSS*bCOD}\right)*\left(160\frac{g}{m^3}\right)}{\left\{1+\left(0.146\frac{g\,VSS}{g\,VSS*day}\right)*\left(16.4\,days\right)\right\}}\right]$$

$$+\left[\frac{\left(0.12\,\frac{g\,VSS}{g\,NH_4-N}\right)*\left(3600\,\frac{m^3}{day}\right)*\left(28.5\,\frac{g}{m^3}\right)}{\left\{1+\left(0.097\frac{g\,VSS}{g\,VSS\,*\,day}\right)*\left(16.4\,days\right)\right\}}\right]$$

$$+\frac{\left[\left(3600\,\frac{m^3}{day}\right)*\left(0.40\,\frac{g\,VSS}{g\,bCOD}\right)*\left(0.15\frac{g}{g}\right)*\left(0.146\,\frac{g\,VSS}{g\,VSS*day}\right)*\left(160\,\frac{g}{m^3}\right)*\left(16.4\,days\right)\right]}{\left[1+\left(0.146\,\frac{g\,VSS}{g\,VSS\,*\,day}\right)*\left(16.4\,days\right)\right]}$$

$$\left(P_{X,BIO}\right)=97007.2272\frac{g}{day}\Rightarrow\left(P_{X,BIO}\right)=97.0072\,\frac{kg}{day}\approx 97.01\,\frac{kg}{day}$$

$$\therefore\left(NO_X\right)=30.00-1.00-\frac{0.12*\left(97.01\frac{kg}{day}\right)*\left(10^3\frac{g}{kg}\right)}{3600\frac{m^3}{day}}$$

[Total ammoniacal nitrogen concentration at effluent is $1\frac{mg}{L}$]

$$\therefore\quad\left(NO_X\right)=\left(30-1-3.234\right)\frac{g}{m^3}\Rightarrow\left(NO_X\right)=25.766\,\frac{g}{m^3}\approx 25.77\,\frac{g}{m^3}$$

Step 8: Check degree of nitrification to determine whether NH4 – N will be removed to a level of $1\frac{g}{m^3}$ in a 2 hour aeration period.

( ) Determine amount of oxidizable N available:

$NO_X = 25.77\,\frac{g}{m^3} = NH_4 - N$ in the feed flow that can be oxidized.

∴ Oxidizable $NH_4 - N$ added/cycle:

$$\left(V_F\right)*\left(NO_X\right)=\left(180\frac{m^3}{Cycle}\right)*\left(25.77\frac{g}{m^3}\right)\Rightarrow\left(V_F\right)*\left(NO_X\right)=4638.6\frac{g}{Cycle}$$

$NH_4 - N$ remaining before fill = $(V_S)*(N_E)$

$$(N_E) = 1\frac{g}{m^3}\ NH_4 - N$$

$$\therefore \quad (V_S)*(N_E) = (V - V_F)*(N_E) = \left\{(600-180)\frac{m^3}{Tank}\right\}*\left(1\frac{g}{m^3}\right) = 420\frac{g}{Tank}$$

$\therefore$ Total oxidizable nitrogen (N) at the beginning of cycle = (4638.6 + 420) g

= 5058.6 g

Initial concentration is obtained by the equation (46)

$$N_O = \left(\frac{5058.6}{600}\frac{g}{m^3}\right) \rightarrow N_O = 8.431\frac{g}{m^3} \approx 8.43\frac{g}{m^3}$$

( ) Determine react time

React time is obtained from the equation (47)

(i) X_N (Nitrifier concentration) is calculated from equation (48)

$$X_N = \left[\frac{\left(0.12\frac{g\,VSS}{g\,NH_4-N}\right)*\left(3600\frac{m^3}{day}\right)*\left(28.5\frac{g}{m^3}\right)*(16.4\ days)}{\left\{1+\left(0.097\frac{g\,VSS}{g\,VSS*day}\right)*(16.4\ days)\right\}*\left(600\ m^3\right)}\right] = 129.9\frac{g}{m^3}$$

$$\mu_{MN}\ (\text{at } 20^{O}\text{C}) = 0.75\frac{gVSS}{gVSS*day}$$

By making use of equation (49), μ_{MN} at 25^{O}C is calculated:

$$\mu_{MN}(at\ 25^{O}C) = \left(0.75\frac{g\,VSS}{g\,VSS*day}\right)*(1.07)^{25-20} \rightarrow \mu_{MN} = 1.052\frac{g\,VSS}{g\,VSS*day}$$

$$K_N\ (\text{at } 20^{O}\text{C}) = \left[\left(0.74\frac{g}{m^3}\right)NH_4 - N\right]$$

Equation (50) is used to obtain K_N at 25^{O}C

$$K_N(at\,25^{O}C) = \left[\left(0.74\frac{g}{m^3}\right)NH_4 - N\right]*(1.053)^{25-20}$$

$$K_N = \left[\left(0.96\frac{g}{m^3}\right)NH_4 - N\right]$$

K_O = Half-saturation constant for DO, $\frac{g}{m^3} = 0.5\frac{g}{m^3}$

Dissolved oxygen concentration, $\frac{g}{m^3}$

(vi) Determine the time for reaction

Solve for t for $N_O = 8.43\ \frac{g}{m^3}$ and $N_E = 1\ \frac{g}{m^3}$

By making use of equation (47), the time required for reaction is calculated here under:

$$\therefore 0.96\ \ln\left(\frac{8.43}{1}\right)+(8.43-1)=\left(129.89\ \frac{g}{m^3}\right)*\left[\frac{\left(1.052\frac{g\ VSS}{g\ VSS * day}\right)}{\left(0.12\frac{g\ VSS}{g\ VSS * NH_4-N}\right)}\right]*\left(\frac{2.0}{2.0+0.5}\right)*t$$

$t = 0.0104\ days = 0.2496\ days = 14.97\ min.$

(c) Determine aeration time

∴ Required aeration time = 15 *min.*

Earlier it was assumed that for 1 complete cycle time required is 1.2 *hours.*

$$\therefore \quad \text{Total aeration time} = \left(\frac{20}{60}+\frac{15}{60*2}\right) hrs = 0.4583\, hrs$$

Step 9: Determine oxygen required/tank using equation (52)

$$R_O = \left(3600\frac{m^3}{day}\right)*\left(160\ \frac{g}{m^3}\right)*\left(\frac{1}{10^3}\ \frac{kg}{g}\right)$$
$$+\ 4.33*\left(3600\frac{m^3}{day}\right)*\left(28.5\ \frac{g}{m^3}\right)*\left(\frac{1}{10^3}\ \frac{kg}{g}\right) - 1.42*\left(97.01\ \frac{kg}{day}\right)$$

$$R_O = 882.5038\ \frac{kg}{day} \approx 882.5\frac{kg}{day}$$

We have calculated that: $\frac{Aeration\,time}{Cycle} = 0.4583\ hrs.$

Number of $\frac{Cycles}{day} = 20$

$$\therefore \quad \text{Total aeration time} = \left(0.4583\ \frac{hrs}{Cycle}\right)*\left(20\frac{Cycles}{day}\right) = 9.2\frac{hrs}{day}$$

Average oxygen transfer rate is calculated from equation (53):

$$\text{Average oxygen transfer rate} = \frac{882.5\frac{kg}{day} of\ O_2}{9.2\frac{hrs}{day}} = 96.3\ \frac{kg}{hr}$$

[**Note:** Oxygen demand will be higher at beginning of aeration period so that aeration system oxygen transfer capacity must be higher than this oxygen transfer rate. Thus oxygen transfer rate should be multiplied by a factor of 1.5 – 2.0 so as to provide sufficient oxygen transfer at the beginning of cycle and to handle peak load.]

Step 11: Determine sludge production using equation (54) [MLSS = X_{TSS}]

Sludge production is calculated by making use of equation (39) and equation (54) is derived; where MLSS = X_{TSS}:

$$(P_{X,TSS}) = \frac{\left(600\frac{m^3}{Tank}\right)*(2\,Tanks)*\left(5000\frac{g}{m^3}\right)*\left(10^{-3}\frac{kg}{g}\right)}{16.4\,days} = 365.85\frac{kg}{day}$$

$$\text{bCOD removed} = \left(7200\frac{m^3}{day}\right)*\left(160\frac{g}{m^3}\right)*\left(10^{-3}\frac{kg}{g}\right) = 1152\frac{kg\,bCOD}{day}$$

$$\text{BOD removed} = \frac{\left(1152\frac{kg}{day}\right)}{\left(1.6\frac{kg\,bCOD}{kg\,BOD}\right)} = 720\frac{kg\,BOD}{day}$$

Step 12: Determine $\left(\frac{F}{M}\right)$ ratio and BOD volumetric loading

(a) $\left(\frac{F}{M}\right)$ Ratio is calculated from equation (58):

$$\left(\frac{F}{M}\right)\text{Ratio} = \left[\frac{\left(3600\,\frac{m^3}{day}\right)*\left(100\,\frac{g}{m^3}\right)}{\left(3050.94\,\frac{g}{m^3}\right)*\left(600\,m^3\right)}\right] = 0.20\frac{g}{g*day}$$

(b) BOD volumetric loading is obtained from equation (59):

$$L_{ORG} = \frac{kg\,BOD}{m^3*day} = \left(\frac{Q*S_O}{V}\right) = \left[\frac{\left(7200\,\frac{m^3}{day}\right)*\left(100\,\frac{g}{m^3}\right)}{\left(10^3\,\frac{kg}{g}\right)*\left(600\,m^3\right)}\right] \rightarrow L_{ORG} = 1.2\frac{kg}{m^3*day}$$

In case of MBR unit, $\left(\frac{F}{M}\right)$ ratio is coming as 0.20. Since the value of $\left(\frac{F}{M}\right)$ ratio ranges in between 0.1 – 0.4 in case of industrial wastewater and the value is within this range. So, the design is satisfactory.

Step 13: DESIGN SUMMARY FOR MEMBRANE BIO REACTOR

Design parameter	*Unit*	**Value**
Average flow	m^3/day	7200
Average BOD load	*kg/day*	720
Average TKN load	*kg/day*	97.01
Number of tanks	*Number*	2
Total aeration time	*hours*	0.49
Cycle time	*hours*	1.2
Total SRT	*day*	16.4
Tank volume	$m^3/Tank$	600
Fill volume/cycle	$m^3/Cycle$	180
Fill volume/Tank volume	*Ratio*	0.3
MLSS	g/m^3	5000
MLVSS	g/m^3	3050.94
(F/M) ratio	*g/(g*day)*	0.20
Volumetric BOD load	$kg/(m^3 * day)$	1.2
Sludge production	*kg/day*	365.85
Average oxygen required/tank	*kg/day*	882.5
Total aeration time/(day*tank)	*hours*	9.2
Average oxygen transfer rate	*kg/hr*	96.3
Number of membrane trains	*Number*	4
Number of Cassettes installed per train	*Number*	3
Number of Membrane modules installed per Cassette	*Number*	40
Maximum number of module spaces available per Cassette	*Number*	48
Total number of Cassettes in plant	*Number*	12
Total number of modules installed in the plant	*Number*	480
Per cent free space available for additional modules	*%*	16.7
Surface are of each membrane module	m^2	31.59
Design net flux – with all trains in operation	$L/(m^2*hr)$	19.79
Design net flux – with all available spaces filled and all trains in operation	$L/(m^2*hr)$	16.49
Membrane Tank dimensions (Preliminary dimensions)	*Length (m) * Breadth (m)*	6.86 * 3.05
Membrane Tank Depth	*Depth (m)*	3.66

2.0 DESIGN OF REVERSE OSMOSIS SKID

The parameters that are available in reverse osmosis skid design are here under:

Parameter	**Concentration**
Temperature *(^oC)*	25 Deg. C
pH	5.5 - 9.0
Oil	1000 – 20000
Total Suspended Solids	200
BOD	1000
COD	1700
Total Sulfides (as S)	235
Phenols	100
Ammonia (as NH_3)	50
Total Dissolved Solids	5000
Organophosphate as PO_4, *mg/L*	10
Conductivity, *micro mho/cm*	9000
M Alkalinity as $CaCO_3$, *mg/L*	2000
Calcium Hardness as $CaCO_3$, *mg/L*	190
Magnesium Hardness as $CaCO_3$, *mg/L*	530
Sodium + Potassium as $CaCO_3$, *mg/L*	2380
Chlorides as Cl, *mg/L*	300
Sulphates (as SO_4), *mg/L*	830
Phosphates + Nitrate as PO_4+NO_3, *mg/L*	78
Ammonia as NH_3, *mg/L*	90
Iron as Fe, *mg/L*	1.0
Total Silica as SiO_2, *mg/L*	25
Reactive Silica as SiO_2, *mg/l*	22.5
SDI	Out of range
$KMnO_4$ consumption at 37 *°C*	10
All Other Metals	Traces

The design of RO skid is done by means of Hydranautics software by using these values mentioned in inside battery limit (ISBL). The specifications are here under:

BASIC DESIGN

Calculation created by: K. Kiran Kumar by HYDRANAUTICS SOFTWARE					
Project name: Reverse osmosis skid design					
HP pump flow	$\frac{m^3}{hr}$	90.7	Permeate flow	$\frac{m^3}{hr}$	68
Recommended pump pressure	bar	17.1	Raw water flow	$\frac{m^3}{hr}$	90.7
Feed pressure	bar	15.9	Permeate recovery	%	75
Feed water temperature	^0C	25	Element age	Years	3
Feed water pH		7.3	Flux age	% per year	7
Chemical Dose [(in ppm), 100%)]	H_2SO_4	0.0	Salt passage increase	% per year	10.0
Acidified feed CO_2		0.01	Feed type	Wastewater	
Average flux rate	$\frac{L}{m^2 * hr}$	20.3			

Stage	Permeate flow m^3/hr	Flow/Vessel		Flux $L/(m^2*hr)$	Beta	Concentration & Throat Pressures		Element Type	Element No:	Array
		Feed m^3/hr	Conc. m^3/hr			bar	bar			
1-1	54.8	9.1	3.6	24.6	1.18	14.7	0.0	LFC3	60	10 * 6
1-2	13.2	7.2	4.5	11.8	1.06	13.5	0.0	LFC3	30	5 * 6

Stage	Element no:	Feed pressure	Pressure drop	Permeate flow	Permeate flow	Beta	Perm Sal TDS	Conc. Osm Pres	Concentrate saturation levels				
		(bar)	*(bar)*	*(m^3/hr)*	*L/(m^2 * hr)*				$CaSO_4$	$SrSO_4$	$BaSO_4$	SiO_2	Lang.
1-1	1	15.9	0.3	1.1	29.1	1.12	33.0	3.0	7	0	0	20	5.7
1-1	2	15.6	0.2	1.0	27.6	1.10	38.1	3.4	8	0	0	23	5.8
1-1	3	15.3	0.2	1.0	25.8	1.14	44.5	3.9	10	0	0	27	5.9
1-1	4	15.1	0.2	0.9	23.9	1.16	51.2	4.6	12	0	0	32	6.0
1-1	5	15.0	0.1	0.8	21.7	1.17	58.8	5.5	15	0	0	37	6.1
1-1	6	14.8	0.1	0.7	19.2	1.18	67.9	6.5	18	0	0	45	6.2
1-2	1	14.5	0.2	0.6	16.3	1.08	73.7	7.2	21	0	0	49	6.3
1-2	2	14.3	0.2	0.5	14.2	1.08	80.2	7.8	23	0	0	53	6.3
1-2	3	14.1	0.2	0.5	12.4	1.07	87.4	8.4	25	0	0	57	6.4
1-2	4	13.9	0.2	0.4	10.7	1.07	95.3	9.1	28	0	0	62	6.4
1-2	5	13.8	0.1	0.3	9.0	1.06	103.9	9.7	30	0	0	66	6.5
1-2	6	13.6	0.1	0.3	7.5	1.05	113.2	10.2	32	0	0	70	6.5

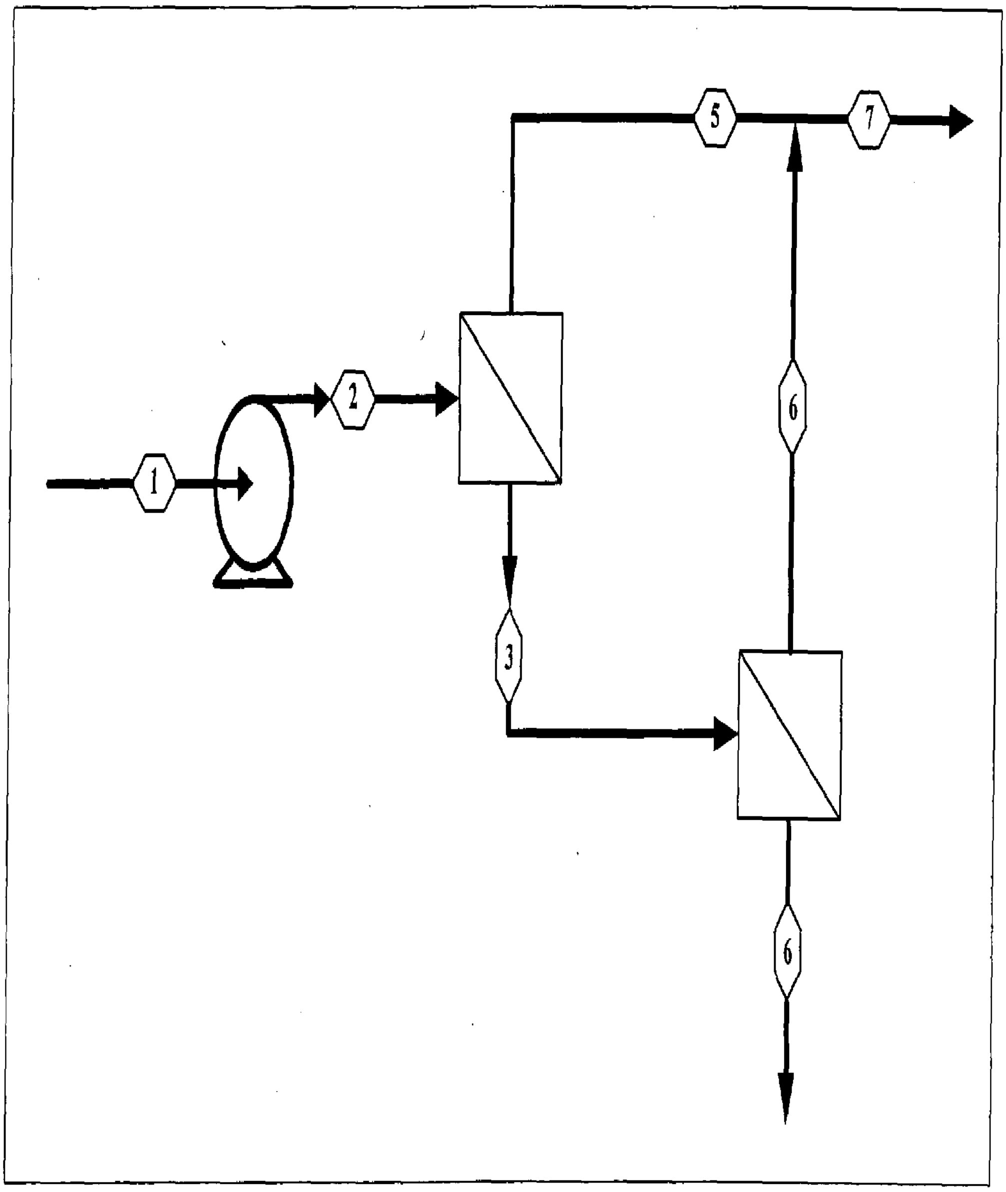
Calculation created by: K. Kiran Kumar by HYDRANAUTICS SOFTWARE					
Project name: Reverse osmosis skid design					
HP pump flow	$\frac{m^3}{hr}$	90.7	**Permeate flow**	$\frac{m^3}{hr}$	68
Recommended pump pressure	bar	17.1	**Raw water flow**	$\frac{m^3}{hr}$	90.7
Feed pressure	bar	15.9	**Permeate recovery**	%	75
Feed water temperature	^0C	25	**Element age**	Years	3
Feed water pH		7.3	**Flux age**	% per year	7
Chemical Dose [(in ppm), 100%)]	H_2SO_4	0.0	**Salt passage increase**	% per year	10.0
Acidified feed CO_2		0.01	**Feed type**	Wastewater	
Average flux rate	$\frac{L}{m^2 * hr}$	20.3			

Stage	**Permeate flow** *m^3/hr*	**Flow/Vessel**		**Flux** *$L/(m^2*hr)$*	**Beta**	**Concentration & Throat Pressures**		**Element Type**	**Element No:**	**Array**
		Feed *m^3/hr*	**Conc.** *m^3/hr*			*bar*	*bar*			
1-1	54.8	9.1	3.6	24.6	1.18	14.7	0.0	LFC3	60	10 * 6
1-2	13.2	7.2	4.5	11.8	1.06	13.5	0.0	LFC3	30	5 * 6

	Raw water		Feed water		Permeate		Concentrate	
Ion	*mg/L*	*meq/L*	*mg/L*	*meq/L*	*mg/L*	*meq/L*	*mg/L*	*meq/L*
Ca	76.2	3.8	76.2	3.8	0.507	0.0	303.2	15.1
Mg	128.8	10.6	128.8	10.6	0.856	0.1	512.6	42.2
Na	1096.0	47.7	1096.0	47.7	34.578	1.5	4280.1	186.1
K	0.0	0.0	0.0	0.0	0.000	0.0	0.0	0.0
NH_4	90.0	5.0	90.0	5.0	3.537	0.2	349.4	19.4
Ba	0.000	0.0	0.000	0.0	0.000	0.0	0.000	0.000
Sr	0.000	0.0	0.000	0.0	0.000	0.0	0.000	0.000
CO_3	114.0	3.8	114.0	3.8	0.356	0.0	454.9	15.2
HCO_3	0.1	0.0	0.1	0.0	0.006	0.0	0.4	0.000
SO_4	830.0	17.3	830.0	17.3	6.467	0.1	3300.6	68.8
Cl	1584.7	44.7	1584.7	44.7	48.926	1.4	6192.0	174.7
F	0.0	0.0	0.0	0.0	0.000	0.0	0.0	0.000
NO_3	78.0	1.3	78.0	1.3	16.665	0.3	262.0	4.2
B	0.0		0.0		0.000		0.00	
SiO_2	25.0		25.0		0.57		98.3	
TDS	5000		4022.7		112.5		15753.5	
pH	7.3		7.3		6.8		7.8	

	Raw water	Feed water	Concentrate
$CaSO_4$/Ksp * 100	6%	6%	33%
$SrSO_4$/Ksp * 100	0%	0%	0%
$BaSO_4$/Ksp * 100	0%	0%	0%
SiO_2 saturation	18%	18%	70%
Langelier saturation index	-0.15	-0.15	1.53
Stiff & Davis saturation index	-0.33	-0.33	0.84
Ionic strength	0.09	0.09	0.33
Osmotic pressure	2.6 bar	2.6 bar	10.2 bar

TWO STAGE SYSTEM



Parameters	Unit	1	2	3	4	5	6	7
Flow	m^3/hr	90.7	90.7	35.9	22.7	54.8	13.2	68.0
Pressure	*bar*	0.0	15.9	14.7	13.5	0.0	0.0	0.0
TDS	*ppm*	4022.7	4022.7	10067.7	15753.5	68.5	295.2	112.5

CHAPTER 6

CAPITAL REQUIREMENTS AND COST ESTIMATION

6.1 CAPITAL REQUIREMENTS AND COSTS

This project broadly covers the following works:

- Collection and transfer of effluent from process units.
- Modifications in API separators, New slop oil transfer pumps and new Catch basin.
- ETP and TTP as per scheme suggested in earlier sections.

[***All cost estimates given in this feasibility report conform to an accuracy level of ± 20%.***]

6.2 TOTAL PROJECT COST

The total capital cost of the proposed project is estimated to be Rupees 102199.5 *Lakhs.* The costs estimates are based on "June 2007 cost level" and do not include any future price escalations.

6.3 BASIS OF ESTIMATES

- All Cost Estimates are based on in-house cost estimates and budgetary cost estimates of the equipments received from the bidders.
- The cost estimates for the OSBL activities for various facilities like piping & pumps for diversion of process effluent streams to new ETP, diversion/modifications of existing storm water sewers/tank farm drains in tank farm areas, diversion of cooling water streams, etc. are based on the cost of similar jobs carried out by EIL for past projects with suitable modifications.
- No cost for building of new approach roads has been considered as the same is not envisaged.
- Indirect cost heads, viz. all taxes and duties etc have been considered as prevalent at June 2007 price level.
- **Contingency:** Overall contingency of 5% is provided to cover various unforeseen events and activities.

- **Chemical Cost:** Supply of all chemicals (except Hydrogen peroxide & Sodium hydroxide) for an initial period of three months during plant commissioning & stabilization has been considered under the scope of the contractor and the same has been capitalized under Capital cost estimate.
- Hydrogen peroxide (H_2O_2) & alkali shall be supplied by HPCL at ETP battery limit during the plant commissioning & stabilization period of three months.

6.4 OPERATING REQUIREMENTS AND COSTS

6.4.1 Fixed Cost

- **Manpower:** There is no change in the already available manpower; existing personnel in various managerial, technical and operator categories shall also operate and maintain the proposed facilities.
- **Repairs and maintenance:** The annual repairs and maintenance cost for proposed facilities are taken at 1% of the capital cost.
- **Insurance:** This is taken as 0.5% of the capital cost.

6.4.2 Variable Cost

- **Utilities:** These include cost of purchased utilities like electricity, Plant air, Instrument air etc. required for the Project. The quantities have been estimated for the Project and the unit rates have been considered from In-house database of EIL.
- **Cost of membranes replacement:** Membrane replacement @ 15% per annum of the total membrane capital cost has been considered towards replacement of membranes.
- **Chemicals:** Various chemicals like Urea, Hydrogen peroxide, Polyelectrolytes, Alum, Caustic soda, Sulphuric acid, etc. shall be used in the Project. The supply of all chemicals for the project is estimated to be Rupees 18.6 *Lakhs* and the same has been included in the Capital cost estimate.

Table 17 and 18 gives the utility and chemicals requirement & total capital cost for the advanced hybrid integrated effluent treatment plant.

Table 17: Utilities and Chemical Consumptions

S. No.	Description	Unit	Consumption
1.	Fresh water	*m^3/day*	5
2.	Low pressure (LP) Steam	*Kg/day*	2400
3.	Instrument air	*nm^3/day*	400
4.	Plant air	*nm^3/day*	800
5.	Power	*KWH*	1300
6.	Alum (100% purity)	*Kg/day*	288
7.	Polyelectrolyte (De-emulsifying)	*Kg/day*	22
8.	H_2O_2 (50%)	*Kg/day*	2688
9.	Antiscalant	*Kg/day*	17
10.	Polyelectrolyte (Dewatering)	*Kg/day*	10
11.	Diammonium phosphate (100%)	*Kg/day*	245
12.	$FeCl_3$	*Kg/day*	144
13.	NaOCl	*Kg/day*	10
14.	Hydrochloric acid	*Kg/day*	125
15.	Alkali	*Kg/day*	500
16.	Sodium bisulphate	*Kg/day*	35
17.	Urea (100%)	*Kg/day*	506

Table 18: Total Capital Cost of the Project

S. No.	Description	Capital Costs (in Rupees *Lakhs*)
1.	Total cost (OSBL Piping/Pumps)	1500.00
2.	Total costs (API Separator modification/New slop oil pumps/New oil catcher)	520.00
3.	Total cost of hybrid integrated effluent treatment plant	5550.00
Total capital expenditure (Rupees Lakhs)		**7570.00**

- The total project cost of Rupees 75.70 *Crores* as specified above <u>excludes</u> consultancy charges for preparation of process package, front end/basic engineering, project management services, etc., which are estimated to be Rs. 5 *Crores*.
- All cost estimates as given above are subject to ± 20% accuracy.

- Taxes like VAT, Service Tax, Work Contract Tax, Octroi shall be extra and shall be to the tune of 35% of total project cost. The total project cost including taxes works out to be **Rs 10219.5 *Lakhs***.
- Duties on imported items have been included.

Capital costs break up is mentioned in the following Tables 19, 20, and 21 respectively.

A. Collection and Transfer of Effluent from Process Units (Under OSBL modifications)

The capital cost of OSBL piping/pumps shall be **Rs. 1500 *Lakhs*** as per the details given below in Table 19.

Table 19: Capital Cost Estimates (OSBL Piping/Pumps)

S. No.	Description	Costs in Rupees (in *Lakhs*)
1.	OSBL Piping	770.00
2.	Pumps and other equipment	618.00
3.	Design and detailed engineering	12.00
4.	Contractor's overhead/Profit/Contingency	100.00
Total (OSBL Piping/Pumps) in Rupees Lakhs		**1500.00**

B. Modifications of API Separator

The capital cost of modifications in existing API separators, new slop oil pumps and a new oil catcher shall be **Rs. 520 Lakhs** as per the details given below in Table 20.

Table 20: Capital Cost Estimates (API Separators, New Slop Oil Pumps and New Oil Catcher)

S. No.:	Description	Costs in Rupees (in *Lakhs*)
1.	New pumps and other requirements	50.00
2.	Civil and Mechanical works	400.00
3.	Cleaning of separators	10.00
4.	Design and detailed engineering	10.00
5.	Contractor's overhead/Profit/Contingency	50.00
Total (API Separators, New Slop Oil Pumps and New Oil Catcher		**520.00**

C. Hybrid integrated effluent treatment plant

- **Capital Cost Estimates for Advanced ETP and TTP** (including two-stage biological treatment system consisting of Sequence Batch Reactor (SBR) & Membrane Bio Reactor (MBR) followed by Reverse Osmosis (RO) modules for tertiary treatment and chemical (H_2O_2) oxidation system for spent caustic treatment) are given below in Table 21.

Table 21: Capital Cost Estimates (for Hybrid Integrated Effluent Treatment Plant)

S. No.:	**Description**	**Costs in Rupees (in *Lakhs*)**
1.	Mechanical works/Equipment costs	7990.00
2.	Civil works	1700.00
3.	Chemicals (for 3 months, excluding H_2O_2 and NaOH	18.00
4.	Electrical works	250.00
5.	Instrumentation works	450.00
6.	ISBL piping	180.00
7.	Other miscellaneous works (e.g., dismantling, warranty costs, etc.)	50.00
Sub - Total (Rupees in *Lakhs*)		**4638.00**
8.	Contractor's overhead/Profit/Contingency	695.00
9.	Design, Detailed engineering, Engineering agency charges, Start – up & commissioning, Financing, Miscellaneous of LSTK contractor	167.00
10.	Membrane (RO + UF) (including Contingency)	50.00
Capital Cost Estimates (for Hybrid Integrated Effluent Treatment Plant)		**5550.00**

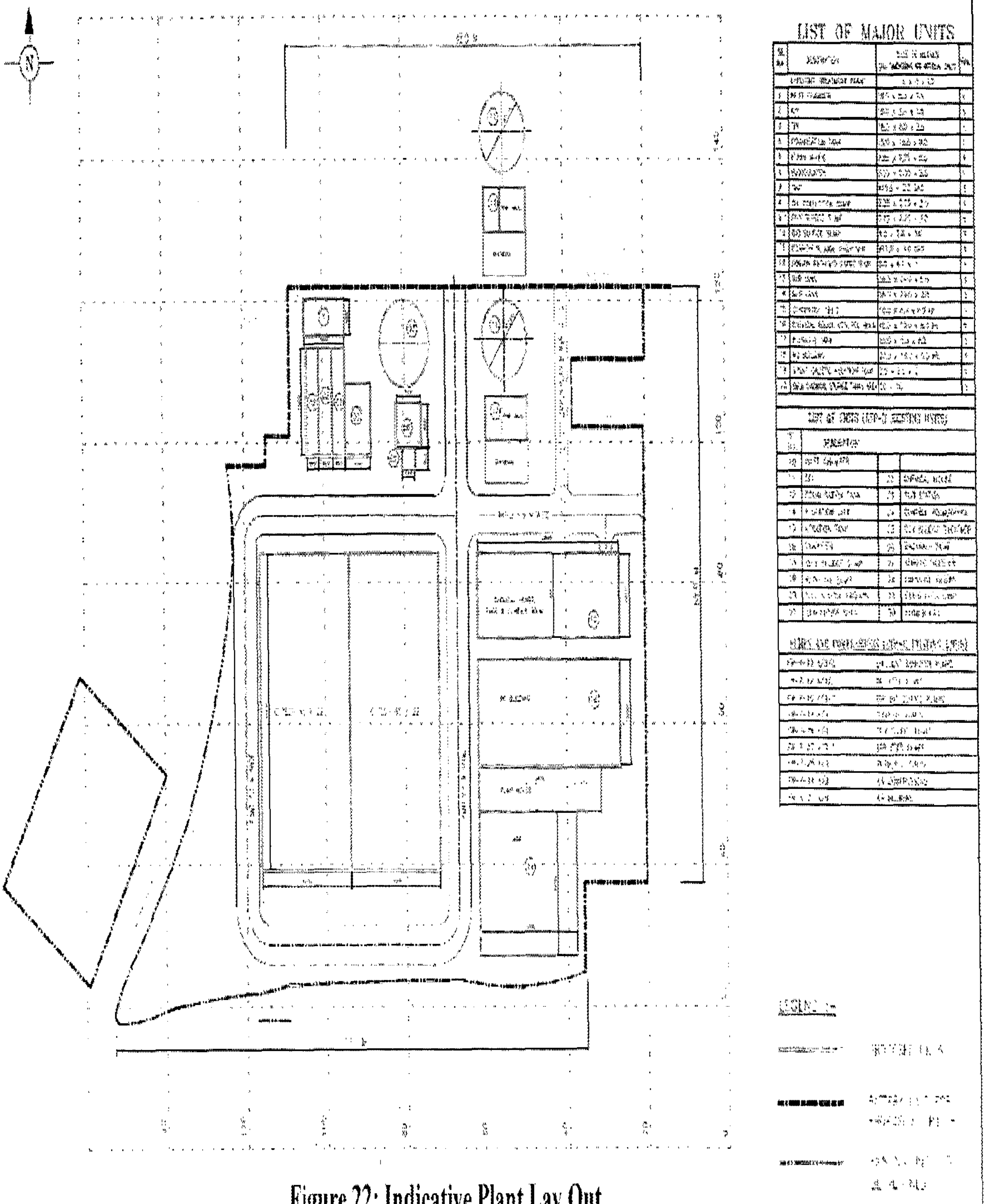


Figure 22: Indicative Plant Lay Out.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The following major conclusion can be drawn from the present work:

- Large volumes of water are used by the petroleum refining industries. Four types of wastewater are produced: surface water runoff, cooling water, process water, and sanitary wastewater.
- Basic approach for wastewater management is minimize generation, adopt segregation, in-situ reuse/recycle treatment, and disposal.
- As the concept of "Zero liquid discharge" has emerged in petroleum refineries so as to obtain all norms required by the regulatory boards, a hybrid integrated effluent treatment system for petroleum refinery has become need of time.
- For effective treatment of the effluent water, the streams are segregated through separate drainage systems and treated accordingly.
- Present wastewater treatment system (WWT) use a combination of trickling filters and activated sludge process (ASP) as a secondary treatment system.
- The use of sequencing batch reactors (SBR), membrane bioreactors (MBR) and reverse osmosis skids have received considerable interest during recent years to overcome the weakness of existing biological treatment system.
- New hybrid integrated effluent treatment system has been presented to meet the requirement of zero discharge and compliance of regulatory parameters.
- This hybrid integrated effluent treatment system meet the DM water parameters so it can be recycled/reused for different purpose such as horticulture, equipment washing, floor washing or in some cases make up water for cooling tower.
- MBRs can handle very high sludge concentrations in the aeration tank because of which the size of aeration tank reduces four to five folds.
- Membranes used in membrane bioreactor (MBR) acts as fine filter, it does not require any further treatment using sand filters, activated carbon filters, etc.

- Total capital cost of the proposed project is estimated to be Rupees 102199.5 *Lakhs*.

7.2 RECOMMENDATIONS

- To maximize the use of treated effluents coming from effluent treatment system.
- To perform cost optimization of the materials in the hybrid integrated effluent treatment system.
- Implementation of sequencing batch reactors (SBR), membranes bio reactors (MBR), reverse osmosis (RO) skids should be done in all the refineries so as to meet the requirement of zero discharge and compliance of regulatory parameters in coming years.
- As membrane bioreactors are very new to petroleum refineries, so exclusive studies on the design of MBR system and pilot plant studies should be done in coming years.

CHAPTER 8

REFERENCES

1. An energy overview of India, (http:/www.fe.doe/international/idiover.html.), 20 October, 2003.
2. Andreev, B. V. and Andrikanis, V. V., *Exhaustive local treatment of refinery effluents to remove hydrogen sulphide and ammonia*, Chemistry and Technology of Fuels and Oils, vol. 42, no. 2, March 2006, pp. 154 – 158.
3. Bagajewicz, M., *A review of recent designs procedures for water networks in refineries and process plants*, Computers and Chemical Engineering, vol. 24, 2000, pp. 2093 – 2113.
4. Barrios-Martinez, A., Barbot, E., Marrot, B., P. Moulin, P., Roche, N., *Degradation of synthetic phenol-containing wastewaters by MBR*, Journal of Membrane Science, 18 April 2006, pp. 288 – 296.
5. Bhattacharya, J. K. and Shekhdar, A. V., *Treatment and disposal of refinery sludges: Indian scenario*, Waste Management and Research, vol. 21, no. 3, June 2003, pp. 249 – 261.
6. Brenneman, D. R. and Hattaway, D. R., *Incorporate Pollution Prevention into your Business Plan*, Hydrocarbon Processing, vol. 4, no. 8, 1995, p. 84.
7. Burks, S. L., *Review of Pollutants in Petroleum Refinery Wastewaters and effect upon Aquatic Organisms*, Environmental International, vol. 7, 11 January 1982, pp. 271 – 283.
8. Chandok, L. K., Tuli, J. M., Mohan, K., Banerjee, A., *Status of Pollution Control in Petroleum Refining Industry*, Chemical Engineering World, 1990, pp. 68 – 85.
9. Chemical Industry Digest, *Upbeat refinery scenario*, January 2007, p. 84.
10. Coelho, A., Castro, A. V., Dezotti, M., G.L. Sant'Anna, G. L. (Jr.), *Treatment of petroleum refinery sour water by advanced oxidation processes*, Journal of Hazardous Materials, 13 March 2006, pp. 178 – 184.
11. Gary and Handwerk, *Petroleum Refining - Technology and Economics*, 3rd Edition, Marcel Dekker, Inc., New York, 1994.

12. Goyal, O. P., *Indian Petroleum Industry: Status, Prospects and Challenges*, Chemical News, May 2006, pp. 41 – 47.

13. Grieves, C. G., Stenstrom, M. K., Walk, J. D., Grutsch, J. F., *Activated Carbon improves Effluent Quality in Refinery Sludge Process*, Industrial Wastes, vol. 23, no. 4, July/August 1977, pp. 30 – 35.

14. Dalmacija, B., Miskovic, D., Zivanov, Z., Petrovic, O., *Combined Microbiological and Advanced Treatment of Oil Refinery and Municipal Wastewaters*, Water Science and Technology, vol. 18, no. 9, 1985, pp. 137 – 146.

15. Dalmaciza, B., Tamas, Z., Karlovic, E., Miskovic, D., *Tertiary Treatment of Oil Field Brine in a bio-sorption system with Granulated Activated Carbon*, Water Research, vol. 30, no. 5, October 1996, pp. 1065 – 1068.

16. Fratila-Apachitei, L. E., Kennedy, M. D., Linton, J. D., Blume, I., Schippers, J. C., *Influence of membrane morphology on the flux decline during dead-end ultrafiltration of refinery and petrochemical wastewater*, Journal of Membrane Science, August 2000, pp. 151 – 159.

17. Guida, J. W, Fruge, D. E., *Improve Wastewater Treatment*, Hydrocarbon Processing, vol. 74, no. 8, 1995, p. 55.

18. Huang, J. C., Hardie, M. G., *Treatment of refinery waste by physicochemical processes*, ASCE J Sanit Eng Div, vol. 97, no. 4, August 1971, pp. 467 – 478.

19. Kaliniichuk, E. M., Makarov, I. A., Vasilenko, I. I., Sukhoverkhova, N. A., *Purification of Petroleum-Refinery wastewaters by Coagulation and Regeneration of the Coagulant Sludge*, All-Union Scientific-Research and Planning-Construction Institute of the Petrochemicals Industry, No. 10, October, 1972, pp. 23 – 27.

20. Katzer, J. R., Michael, P. R., Spare, A. V., *Petroleum Refining: Poised for Profound Changes*, Chemical Engineering Progress, July 2000, p. 41.

21. Lee, L. Y., Hu, J. Y., Ong, S. L., Ng, W. J., Ren, J. H., Wong, S. H., *Two-stage SBR for treatment of oil refinery wastewater*, Water Science and Technology, vol. 50, no. 10, 2004, pp. 243 – 249.

22. Leffler, W. L., *Petroleum Refining for the Non-Technical Person*, 2nd Edition, PennWell Publishing Company, Tulsa, Oklahoma, 1985.

23. Mall, I. D., *Petrochemical Process Technology*, Macmillan India Limited, 1st Edition, p. 70.

24. Miranda, J. G., *Designing parallel – plate separators*, Chemical Engineering, 1977, vol. 84, pp. 105 – 107.

25. Moreno, C., Farahbakhshazad, N., Morrison, G. M., *Ammonia removal from oil refinery effluent in vertical upflow macrophyte column systems*, Water, Air, and Soil Pollution, vol. 135, no. 1 – 4, 2002, pp. 237 – 247.

26. Moursy, A. S. and Abo El-Ela, S. E., *Treatment of Oily Refinery Wastes using a Dissolved Air Floatation Process*, Environmental International, vol. 7, 1982, pp. 267 – 270.

27. *Petroleum Refinery Enforcement Manual*, U.S. EPA Office of Enforcement by PEDCo Environmental Inc., Arlington, Texas, March 1980.

28. *Petroleum Refining*, Petroleum Prevention and Abatement Handbook, WORLD BANK GROUP, p. 377.

29. Pirog, R., *Petroleum Refining: Economic Performance and Challenges for the Future*, p. 1

30. Rajkumar, D., Palanivelu, K., *Electrochemical treatment of industrial wastewater*, Journal of Hazardous Materials, 4 August 2004, pp. 123 – 129.

31. Ram Prasad, *Petroleum Refining Technology*, Khanna Publishers, 1st Edition, March 2000.

32. Rao, V. V. S. G., Dhar, R. L., Khoker, C. S., *Mass Transport Modeling for Assessment of Groundwater contamination around Mathura Oil Refinery, Mathura, Uttar Pradesh, India*, Environmental Geology, 12 July 1999, pp. 1138 – 1146.

33. Rigas, F., Panteleos, P., Laoudis, P., *Central Composite Design in a Refinery Wastewater Treatment by Air Floatation*, Global Nest: the International Journal, vol. 2, no. 3, March 2000, pp. 245 – 253.

34. Sagane, A. N., *Responsible Care in Action - A Case Study of Effluent Treatment and Recycle at Reliance - Patalganga*, Industrial Safety Chronicle, January/March, 2003, pp. 57 – 62.

35. Saifutdinov, K. Z., Gerber, V. Ya., Ioakimis, E. G., Efimova, A. K., *Treatment of Refinery Wastewater and Return to Circulating Water system*, Chemistry and Technology of Fuels and Oils, vol. 10, no. 11 – 12, November/December 1974, pp. 922 – 927.

36. Siegel, J. H., *Control VOC Emissions*, Hydrocarbon Processing, vol. 76, no. 4, 1997, p. 119.

37. Singh, I. J., *Indian Refining Industry*, Hydrocarbon Engineering, vol. 7, no. 1, January 2002, p. 10.

38. Stutz, C. N., *Industrial Wastes Manual*, 1st Edition, Bringham Young University, 1972.

39. Tchobanoglous, G., Burton, F. L., Stensel, H. D., *Wastewater Engineering*, Fourth edition, Tata McGraw-Hill Publishing Company Limited, p. 423.

40. Teodosiu, C. C., Kennedy, M. D., Van Straten, H. A., Schippers, J. C., *Evaluation of Secondary Refinery Effluent Treatment using Ultrafiltration Membranes*, Water Research, vol. 33, no. 9, September 1999, pp. 2172 – 2180.

41. Tyagi, R. D., Tran, F. T., Chowdhury, A. K. M. M, *Biodegradation of Petroleum Refinery wastewater in a Modified Rotating Biological contactors with polyurethane foam attached to the* disks, Water Research, vol. 27, no. 1, May 1993, pp. 91 – 99.

42. UNEP, *Water and Wastewater Reuse - An Environmentally Sound Approach for Sustainable Urban Water Development*, pp. 11 – 13.

43. Vaiopoulou E., Melidis, P., Aivasidis, A., *Sulphide removal in Wastewater from Petrochemical and Petroleum industries by Autotrophic Denitrification*, Water Research, vol. 39, 2 September 2005, pp. 4101 – 4109.

44. Vigneswaran, S. and Visvanathan, C., *Water Treatment Process*, CRC Press, pp. 27 – 41.

45. Wang, J. M., *Petrochemicals*, Water Environment Research, vol. 70, no. 4, 1998, p. 658.

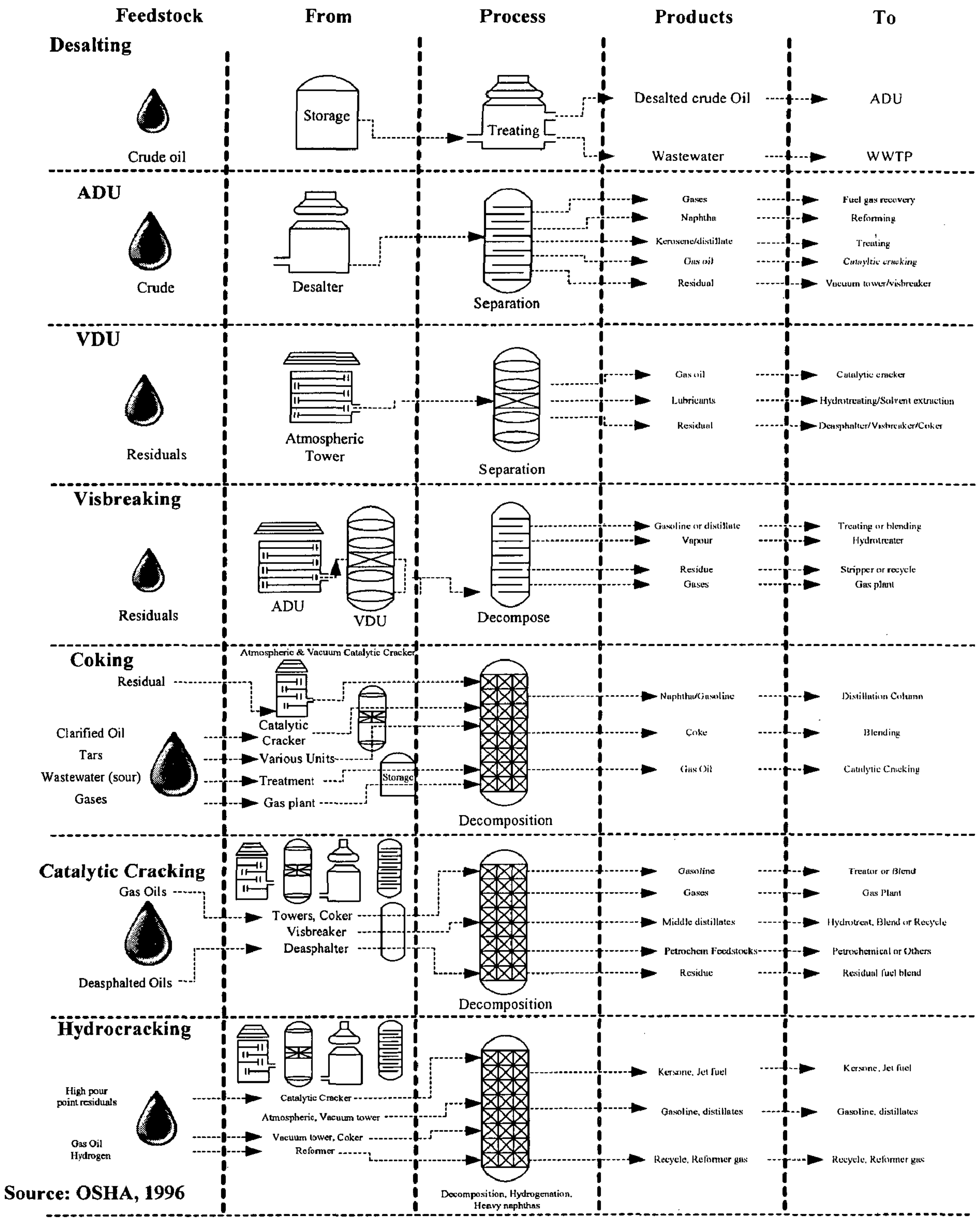
46. Yuan, W., Stenstrom, M. K., Ozgur, N. H., Okrent, D., *An Integrated Expert System for Operating a Petroleum Refinery Activated Sludge Process*, University of California, Los Angeles, 1991, pp. 480 – 485.

47. Zbontar, L. and Glavic, P., *Total site: Wastewater minimization, Wastewater reuse and regeneration reuse*, Resources, Conservation and Recycling, vol. 30, 7 April 2000, pp. 261 – 275.

48. Zhong, J., Sun, X., Wang, C., *Treatment of oily wastewater produced from refinery processes using flocculation and ceramic membrane filtration*, Separation and Purification Technology, vol. 32, 2003, pp. 93 – 98.

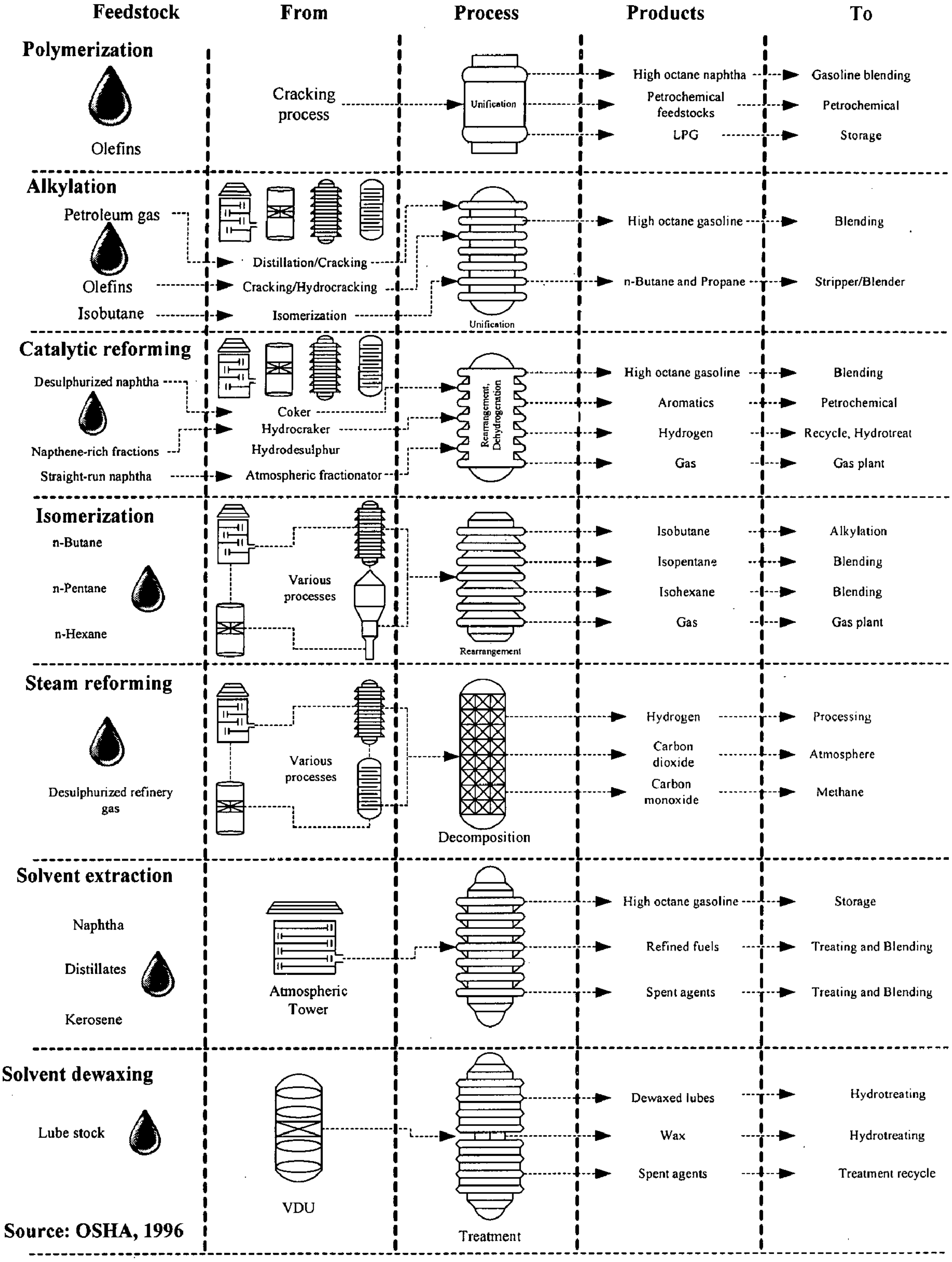
49. *http://www.osha.gov/dts/osta/otm/otm_iv/otm_iv_2.html*

REFINERY PROCESSES



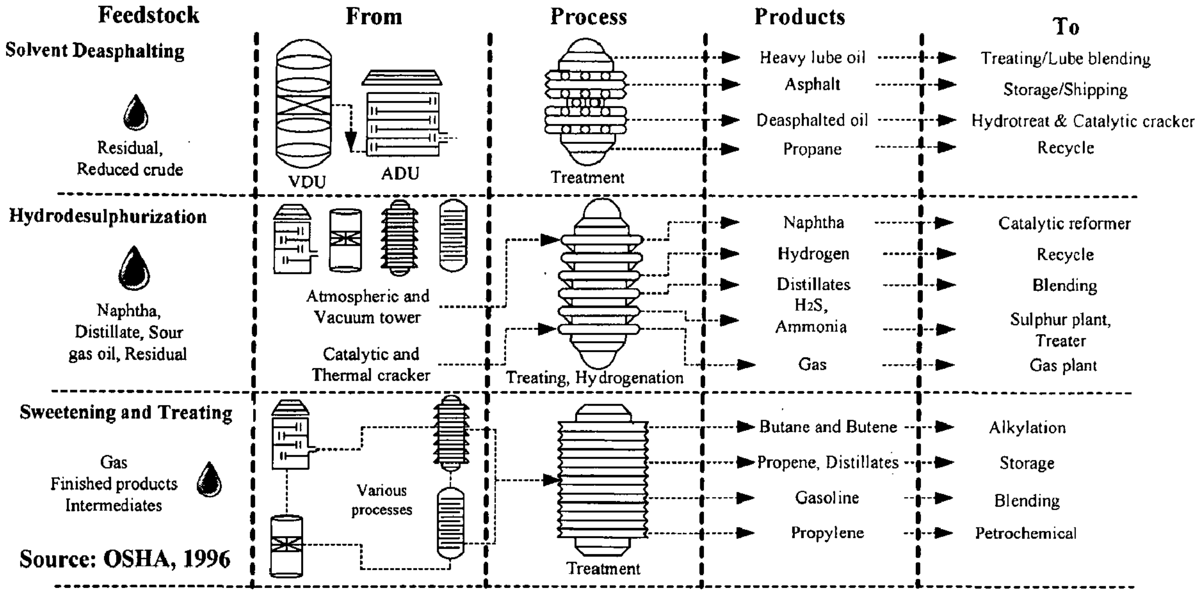
Source: OSHA, 1996

Figure 22: Simplified Block Diagram of Petroleum Refinery Processes.



Source: OSHA, 1996

Figure 22: Simplified Block Diagram of Petroleum Refinery Processes (Contd.).



Source: OSHA, 1996

Figure 22: Simplified Block Diagram of Petroleum Refinery Processes (Contd.).

Appendix 2

WASTEWATER TREATMENT PLANT EQUIPMENT BLOCK DIAGRAM

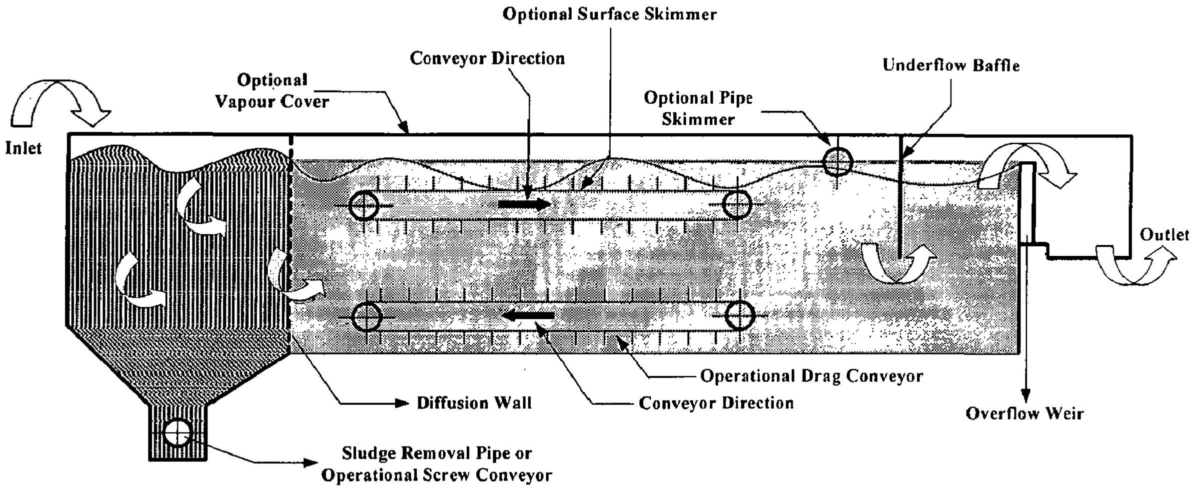


Figure 23: API Separator Flow Diagram.

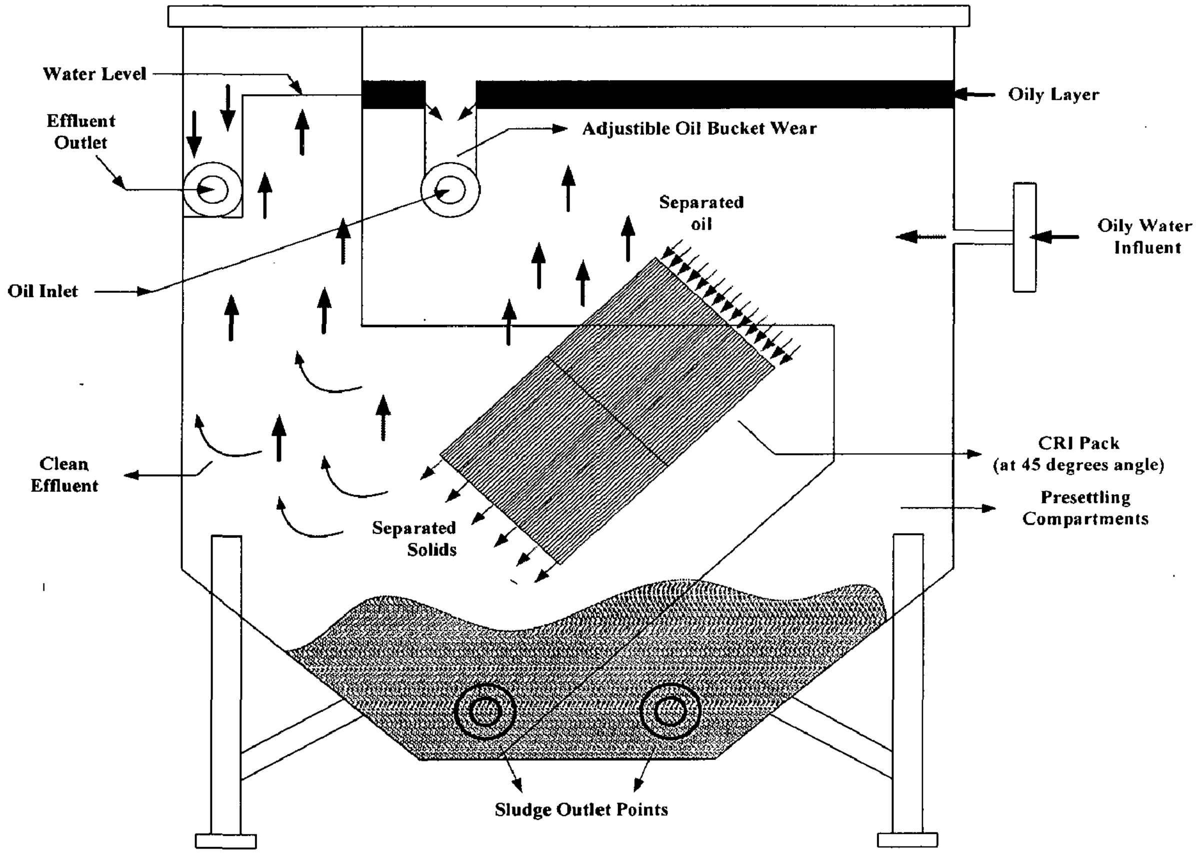


Figure 24: Tilted Plate Interceptor (TPI)/Corrugated Plate Interceptor (CPI) Flow Diagram

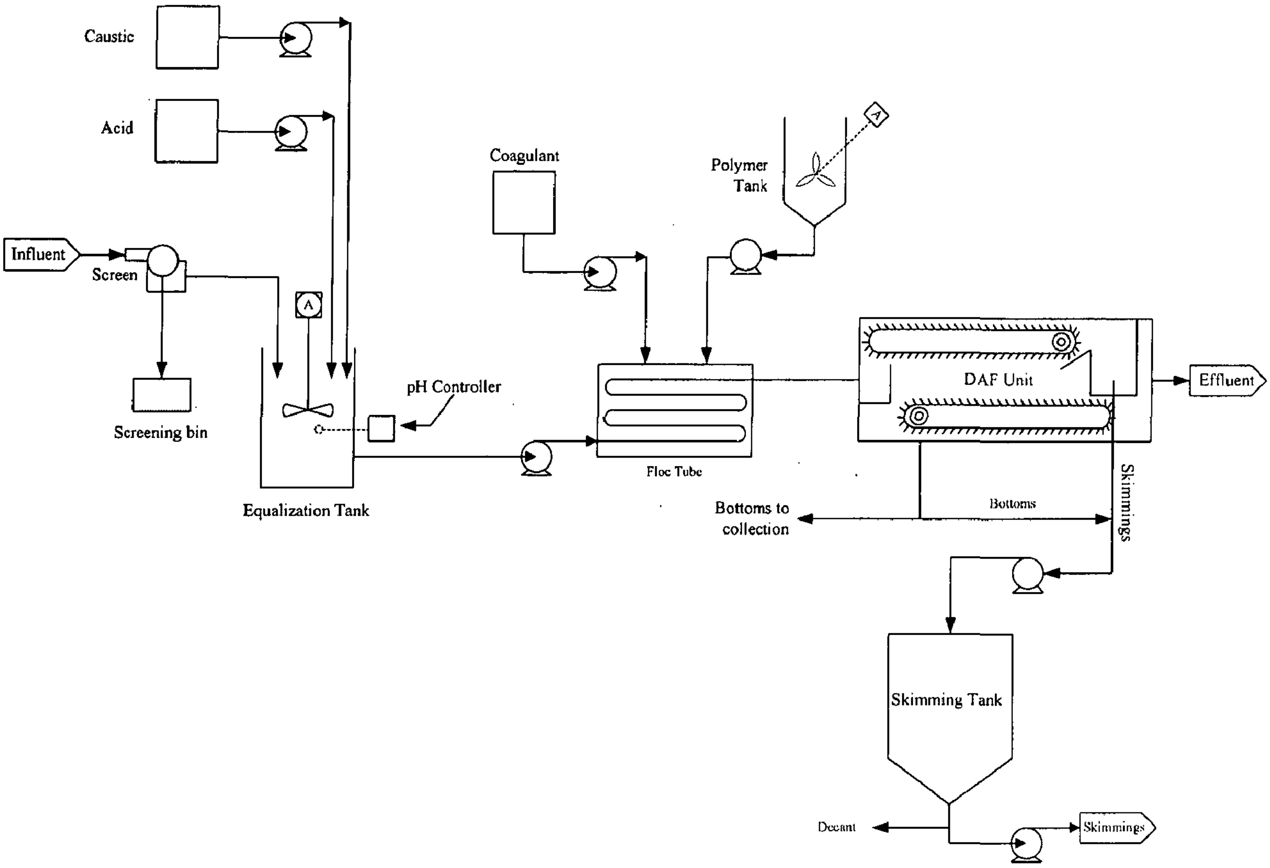


Figure 25: Dissolved Air Flotation (DAF) Process Flow Diagram.

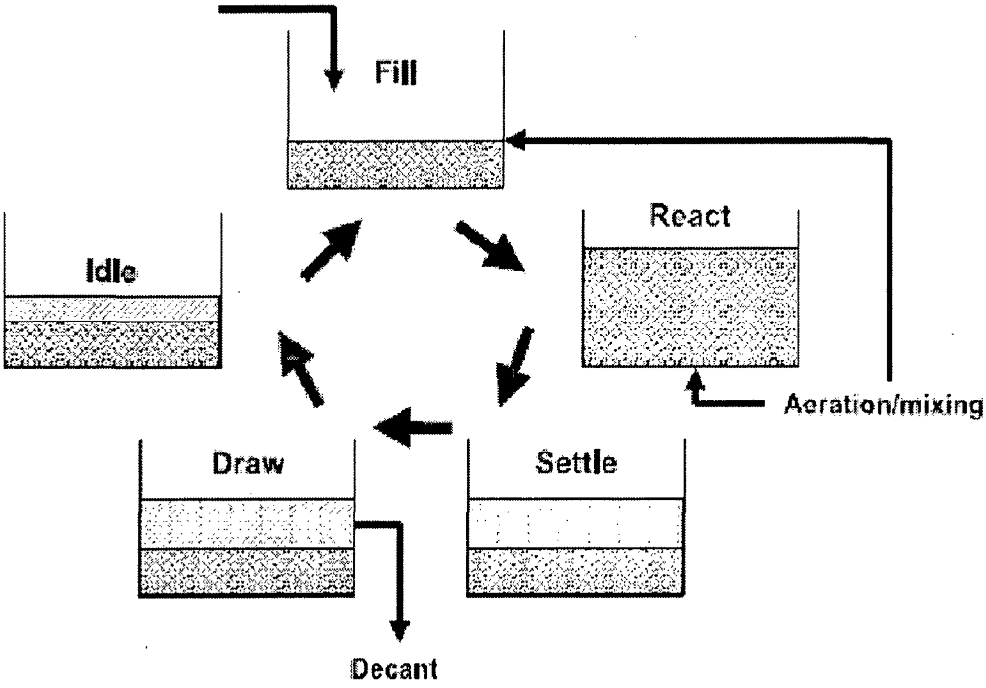


Figure 26: Sequencing Batch Reactor (SBR) Process Flow Diagram.

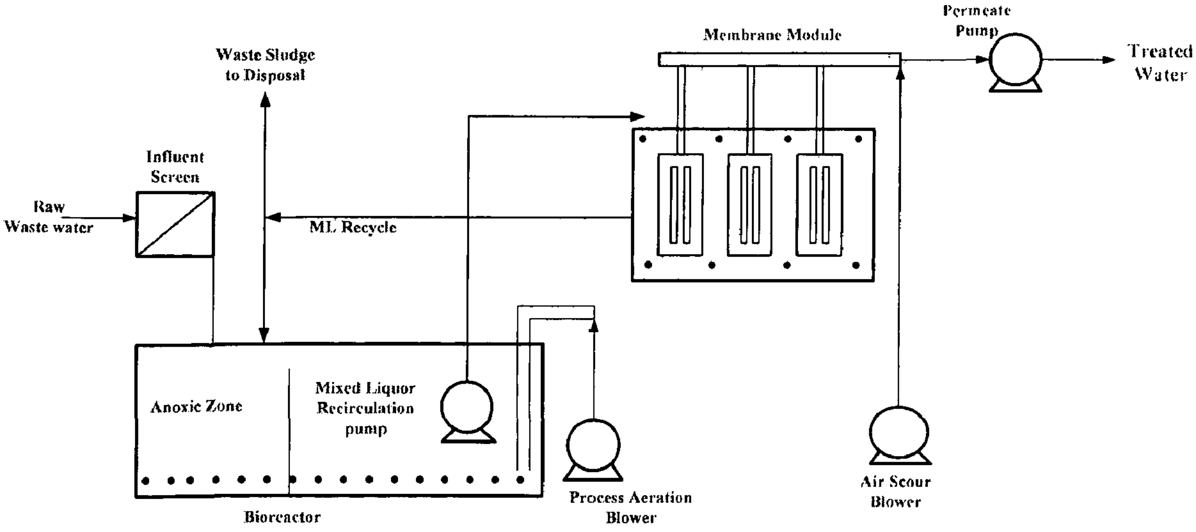


Figure 27: Simplified Membrane Bioreactor (MBR) Plant.

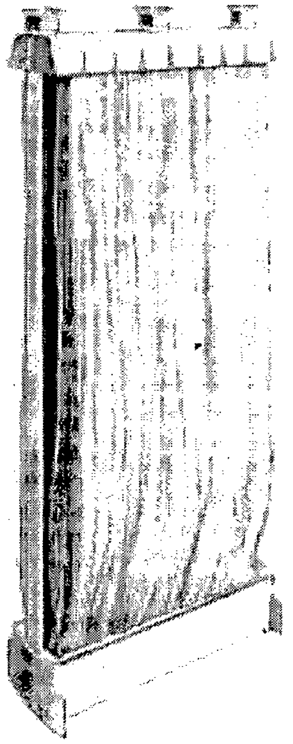
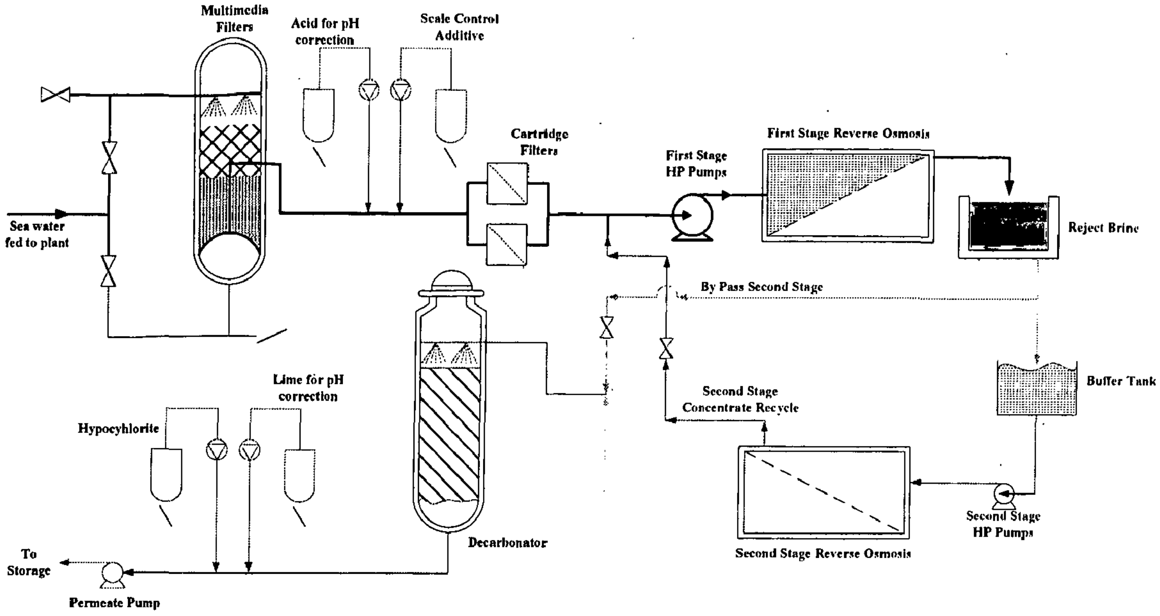
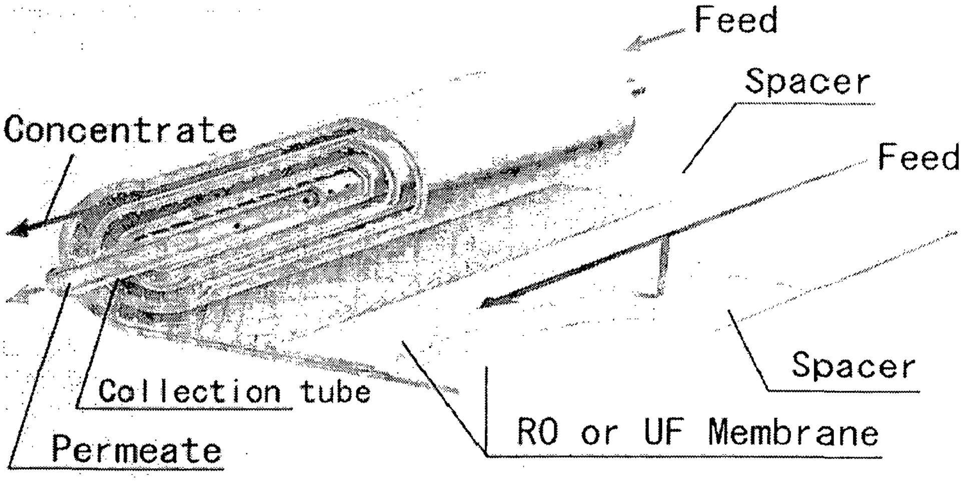


Figure 28: Membrane Bioreactor (MBR) Module.



Source: Smith and Shah, 1994

Figure 29: Diagram of Simplified Reverse Osmosis Skid.



[**Source:** UNEP, Water and Wastewater reuse]

Figure 30: Reverse Osmosis Membrane Module