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THEME

Technical Evaluation and Process Optimization of the Refinery Oily Wastewater Treatment System: Proposal for a Controlled Dilution Tank»

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Dedication

Every achievement begins with the support of sincere hearts, the warmth of endless prayers, and the presence of those who never stopped believing in us.

With immense gratitude and heartfelt affection, I dedicate this humble work to the most precious people in my life.

To my beloved father, ***Benaissa****,*

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CONTENTS

ABSTRACT

This work deals with the treatment of oily wastewater generated by a petroleum refinery. Refinery effluents are complex industrial wastewaters that may contain hydrocarbons, suspended solids, organic matter, ammonia, sulfides, phenols, salts, and solvent-related compounds such as furfural. These pollutants can affect the environment and disturb the performance of treatment units, especially biological treatment.

The study focuses on the characterization of refinery oily wastewater, the evaluation of the existing treatment systems, and the proposal of a technical improvement based on engineering principles and analytical data. The proposed improvement consists of a controlled dilution tank using recycled treated water, followed by gradual re-feeding to the biological treatment, in order to reduce the impact of high-organic-load and furfural-related shock events.

Keywords: refinery wastewater, oily wastewater, furfural, wastewater treatment, controlled dilution, process optimization.

ملخص

يتناول هذا العمل معالجة المياه العادمة الزيتية الناتجة عن مصفاة بترولية. تُعد مياه الصرف الخاصة بالمصافي مياهًا صناعية المعقدة، إذ قد تحتوي على الهيدروكربونات، المواد العالقة، المواد العضوية، الأمونيا، الكبريتيدات، الفينولات، الأملاح، وبعض المركبات المرتبطة بالمذيبات مثل الفورفورال. يمكن لهذه الملوثات أن تؤثر على البيئة وتسبب اضطراباً في أداء وحدات المعالجة، خاصة المعالجة البيولوجية.

تركز الدراسة على توصيف المياه الزيتية للمصفاة، وتقييم أنظمة المعالجة الموجودة، واقتراح تحسين تقني اعتماداً على مبادئ هندسية وبيانات تحليلية. يتمثل التحسين المقترح في استعمال خزان تخفيف متحكم فيه باستعمال مياه معالجة معاد تدويرها، ثم إعادة إدخال المياه تدريجياً إلى المعالجة البيولوجية، بهدف تقليل تأثير الصدمات ذات الحمل العضوي المرتفع والمرتبطة بالفورفورال.

الكلمات المفتاحية :مياه المصافي، المياه الزيتية، الفورفورال، معالجة المياه المستعملة، التخفيف المتحكم فيه، تحسين العمليات.

RESUME

Ce travail porte sur le traitement des eaux huileuses générées par une raffinerie de pétrole. Les effluents de raffinerie sont des eaux industrielles complexes pouvant contenir des hydrocarbures, des matières en suspension, de la matière organique, de l’ammoniac, des sulfures, des phénols, des sels, ainsi que des composés liés aux solvants tels que le furfural. Ces polluants peuvent affecter l’environnement et perturber le fonctionnement des unités de traitement, en particulier le traitement biologique.

L’étude vise à caractériser les eaux huileuses de raffinerie, à évaluer les systèmes de traitement existants et à proposer une amélioration technique basée sur des principes d’ingénierie et des données analytiques. L’amélioration proposée consiste en un réservoir de dilution contrôlée utilisant de l’eau traitée recyclée, suivi d’une réintroduction progressive vers le traitement biologique, afin de réduire l’impact des chocs à forte charge organique et liés au furfural.

Mots-clés : eaux usées de raffinerie, eaux huileuses, furfural, traitement des eaux usées, dilution contrôlée, optimisation des procédés.

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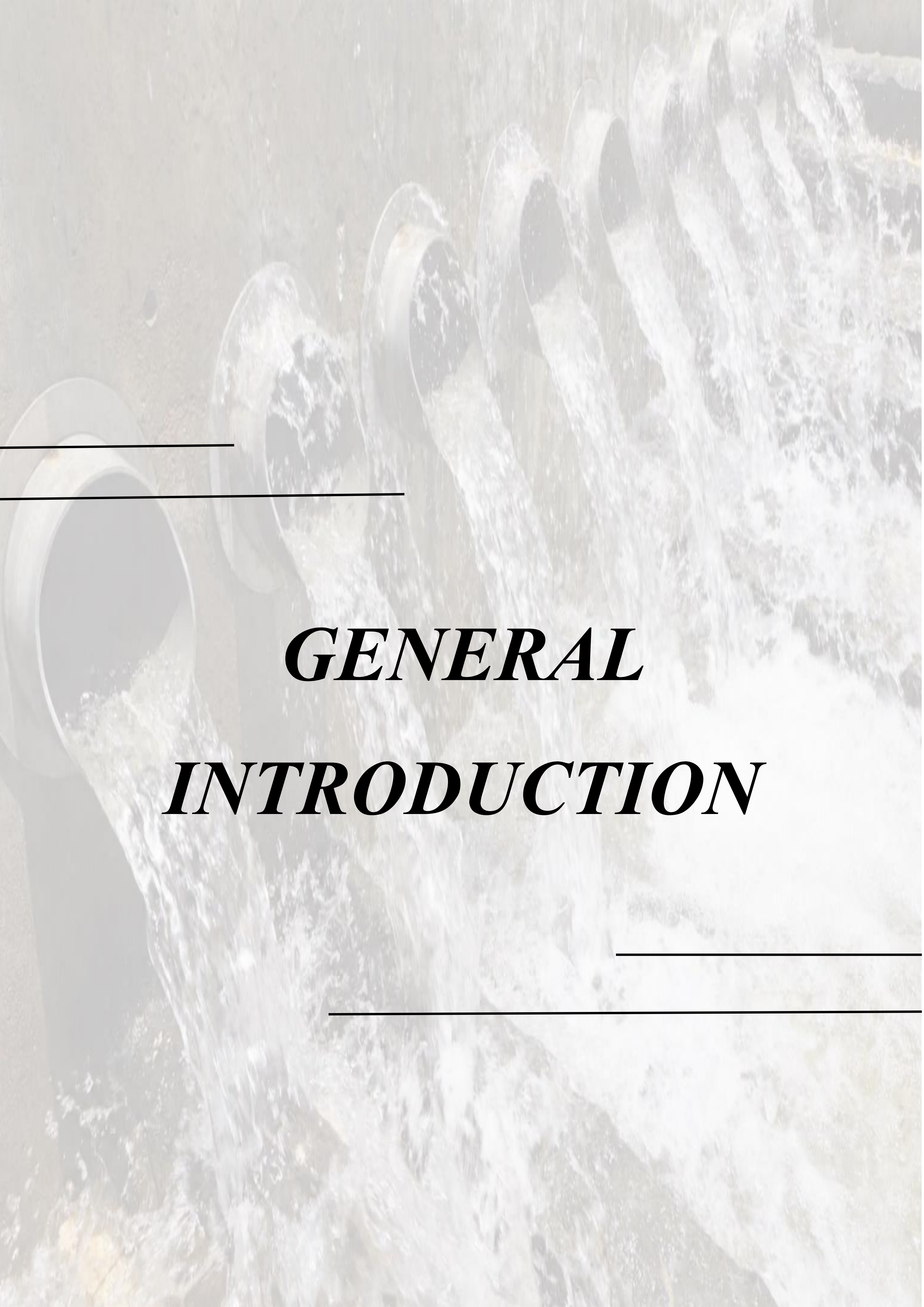
SYMBOLS AND ABBREVIATIONS

Abbreviations :

Abbreviation	**Meaning**
API	American Petroleum Institute / API oil-water separator
BOD_5	Biochemical Oxygen Demand after 5 days
COD	Chemical Oxygen Demand
DBO_5	Demande Biochimique en Oxygène après 5 jours
DCO	Demande Chimique en Oxygène
DO	Dissolved Oxygen
EGF	Enhanced Gas Flotation
HC	Hydrocarbons
HRT	Hydraulic Retention Time
IGF	Induced Gas Flotation
MEK	Methyl Ethyl Ketone
MES	Matières En Suspension
NH_3	Ammonia
O&G	Oil and Grease
pH	Potential of Hydrogen
PO_4^{3-}	Phosphate ion
RA1/Z	Arzew Refinery
SBR	Sequencing Batch Reactor
STEP	Station d'Épuration
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
WTP	Wastewater Treatment Plant

Symbols :

Symbol	Meaning	Unit
C	Pollutant concentration	mg/L or ppm
Cb	Concentration of the polluted batch before dilution	mg/L or ppm
Cd	Concentration of the dilution water	mg/L or ppm
Cfinal	Final concentration after dilution	mg/L or ppm
Cin	Inlet concentration	mg/L or ppm
Cout	Outlet concentration	mg/L or ppm
Ctarget	Target concentration	mg/L or ppm
L	Pollution load	kg/day
Q	Flow rate	m^3/h or m^3/day
t	Time / hydraulic retention time	h
V	Volume	m^3
Vb	Volume of the polluted batch	m^3
Vd	Volume of dilution water	m^3
Vtotal	Total volume after dilution	m^3
η	Removal efficiency	%



GENERAL INTRODUCTION

General Introduction

Water quality protection has become one of the major environmental challenges associated with modern industrial development. Although water is essential for human activities, ecosystems, agriculture, and economic growth, its quality is increasingly affected by domestic, urban, agricultural, and industrial discharges. Untreated or insufficiently treated wastewater can introduce organic matter, nutrients, suspended solids, toxic substances, hydrocarbons, and persistent pollutants into receiving environments. This deterioration can disturb aquatic ecosystems, reduce the availability of safe water resources, and increase risks to public health and environmental sustainability [1], [2].

Industrial wastewater represents a particular concern because its composition is often complex, variable, and strongly dependent on the nature of the production process. Among industrial sectors, petroleum refining is recognized as a major generator of contaminated wastewater due to the large quantities of water used in desalting, washing, cooling, steam generation, process operations, equipment cleaning, and maintenance activities. Refinery effluents may contain oil and grease, suspended solids, dissolved and emulsified hydrocarbons, phenols, sulfides, ammonia, salts, heavy metals, and other organic and inorganic pollutants. These compounds contribute to high chemical oxygen demand (COD), biological oxygen demand (BOD_5), toxicity, turbidity, salinity, and operational instability in treatment systems. Depending on refinery operations, solvent-related compounds such as furfural and MEK may also appear in specific wastewater streams and may affect biological treatment if not properly controlled [3], [4], [5].

Oily wastewater is one of the most important and difficult refinery effluent streams to manage. The difficulty of its treatment is related not only to the concentration of oil, but also to the form in which hydrocarbons are present. Oil may occur as free oil, dispersed droplets, emulsified oil, or dissolved hydrocarbon compounds. While free oil can generally be removed by gravity separation, dispersed and emulsified fractions require more advanced physical, chemical, or biological treatment steps. If discharged without adequate treatment, oily wastewater can form films on the water surface, reduce oxygen transfer, affect aquatic organisms, contaminate soil and groundwater, and disturb the performance of downstream biological treatment units [3], [5], [6].

For this reason, refinery wastewater treatment is generally based on a combination of successive processes rather than a single treatment operation. Preliminary and primary treatment are commonly used to remove coarse solids, grit, free oil, grease, and a significant part of suspended matter through screening, sedimentation, oil-water separation, coagulation-flocculation, and flotation. Secondary biological treatment is then applied to reduce biodegradable organic matter and nitrogenous compounds, commonly through activated sludge systems or sequencing batch reactors. Tertiary or polishing treatment, such as filtration, may be required to improve final effluent quality and comply with discharge or reuse requirements [5], [7], [8].

In refinery wastewater treatment plants, maintaining stable performance is challenging because the flow rate and pollutant load can vary significantly with production conditions, rainfall events, cleaning operations, maintenance activities, and accidental releases. Sudden increases in oil and grease, suspended solids, organic load, salinity, or toxic compounds may reduce the efficiency of separation, flotation, and biological treatment. In addition, insufficient aeration, inadequate chemical dosing, nutrient imbalance, poor sludge settleability, or unsuitable hydraulic retention time can negatively affect treatment performance. Therefore, a reliable evaluation of refinery wastewater treatment requires both an understanding of the treatment process and the use of operational and analytical data [4], [7], [8].

The present work is carried out in the context of oily wastewater treatment in a petroleum refinery. The refinery treatment system includes several stages designed to progressively reduce hydrocarbons, suspended solids, organic matter, and other pollutants before discharge or possible reuse. The study focuses on describing the existing treatment chain, analyzing the characteristics of refinery effluents, distinguishing between influent load characterization and outlet quality assessment, evaluating treatment performance using analytical data and regulatory references, and proposing a technically justified improvement. This approach is supported by refinery operating documentation, scientific literature, engineering design references, and available analytical data [9], [10] .

The objective of this thesis is to study the treatment of oily wastewater generated by a petroleum refinery and to propose a technical improvement supported by engineering analysis. The work aims to establish a clear understanding of the origin and characteristics of refinery wastewater, describe the treatment processes used in the industrial site, evaluate the existing treatment systems using analytical data, regulatory comparison, and engineering calculations, and propose a technical improvement for better control of shock loads.

This thesis is organized into three chapters. The first chapter presents the general background of water pollution, wastewater characteristics, petroleum refinery wastewater, oily wastewater, and the main treatment technologies used for such effluents. The second chapter introduces the industrial site and describes the refinery wastewater treatment processes, with emphasis on the treatment sequence and the role of each unit operation and the third chapter evaluates the existing effluent treatment systems using the selected monthly analytical data, regulatory comparison, pollutant-load calculations, and biodegradability interpretation. It also identifies the main treatment limitation and proposes a controlled dilution and gradual re-feeding solution to protect biological treatment from furfural-rich and high-organic-load shock events, using available data and appropriate engineering criteria.

By combining industrial case study information, wastewater treatment engineering, by combining industrial case study information and wastewater treatment engineering, this work seeks to develop a professional. The study is intended to contribute to better process understanding, more reliable performance evaluation, and the identification of a practical improvement option adapted to refinery wastewater characteristics and existing treatment constraint.

CHAPTER ONE

General Background on Water Pollution and Refinery Oily Wastewater

CHAPTER I: General Background on Water Pollution and Refinery Oily Wastewater

I.1 Introduction

Water pollution is a major environmental issue associated with urbanization, agricultural activity, and industrial development. Wastewater discharged without adequate treatment may contain organic matter, suspended solids, nutrients, salts, hydrocarbons, metals, and toxic compounds, which can deteriorate the physical, chemical, and biological quality of receiving waters [1], [2].

Industrial wastewater is particularly important because its composition is often complex and variable. Unlike domestic wastewater, it depends on raw materials, production processes, cleaning operations, utilities, and accidental releases. Therefore, its treatment requires proper characterization, segregation, monitoring, and process-specific treatment strategies [8].

Petroleum refineries generate wastewater from desalting, washing, cooling, steam production, process operations, equipment cleaning, and drainage systems. These effluents may contain oil and grease, hydrocarbons, suspended solids, phenols, sulfides, ammonia, salts, and other pollutants that can increase COD, BOD_5, turbidity, toxicity, and biological treatment inhibition [3], [4], [5].

This chapter presents the theoretical background required to understand refinery oily wastewater treatment. It discusses water pollution, industrial wastewater, wastewater quality parameters, petroleum refinery wastewater, oily wastewater characteristics, environmental and operational impacts, and the main treatment technologies used for such effluents.

I.2 Water Pollution and Industrial Wastewater

I.2.1 Concept of Water Pollution

Water pollution can be defined as the degradation of water quality caused by the introduction of substances or energy that modify its natural characteristics and make it less suitable for ecological, domestic, agricultural, industrial, or recreational uses. Pollution may affect surface water, groundwater, coastal water, and aquatic ecosystems. It may be visible, such as turbidity, color, foam, floating solids, or oil films, but it may also be invisible when contaminants are dissolved or present at low concentrations.

From an environmental point of view, water pollution is not limited to the presence of undesirable substances. It also includes any change that disturbs the natural balance of aquatic systems. Organic matter can reduce dissolved oxygen, nutrients can promote eutrophication, toxic substances can affect aquatic organisms, and persistent pollutants can accumulate in sediments and living tissues [2], [8].

In wastewater engineering, pollution is evaluated using parameters such as pH, temperature, TSS, turbidity, COD, BOD_5, TDS, oil and grease, nitrogen compounds, phosphorus compounds, phenols, sulfides, and specific toxic substances. These parameters are used to characterize wastewater, estimate pollution loads, select treatment processes, and evaluate treatment efficiency [8].

I.2.2 Main Sources of Water Pollution

Water pollution sources can be classified according to their origin and the type of contaminants they introduce into the aquatic environment. The main categories are domestic wastewater, agricultural runoff, urban runoff, and industrial wastewater. This classification is useful because each source has specific pollutant characteristics and requires different prevention, control, and treatment strategies [1], [2].

The main sources of water pollution can be summarized as follows:

I.2.2.1 Domestic wastewater

Domestic wastewater is generated from households, public buildings, offices, schools, hospitals, and sanitary facilities. It usually contains biodegradable organic matter, suspended solids, nutrients, detergents, fats, oils, grease, and microorganisms. Its main environmental effects are oxygen depletion, eutrophication, and microbial contamination of receiving waters [1].

I.2.2.2 Agricultural runoff

Agricultural runoff is produced when rainwater or irrigation water flows over cultivated land, livestock areas, or fertilized soils. It may carry nitrates, phosphates, pesticides, herbicides, sediments, and organic residues into surface water or groundwater. This type of pollution is often diffuse and difficult to control because it does not usually originate from a single discharge point [2], [8].

I.2.2.3 Urban runoff

Urban runoff is generated when rainfall washes roads, parking areas, roofs, industrial zones, and drainage networks. It can transport suspended solids, hydrocarbons, heavy metals, plastics, rubber particles, and other contaminants. In areas where stormwater networks are connected to industrial or oily surfaces, runoff can become a significant source of hydrocarbon pollution [2], [8].

I.2.2.4 Industrial wastewater

Industrial wastewater is generated by production processes, utilities, washing operations, cooling systems, equipment cleaning, and accidental releases. Its composition depends strongly on the type of industry, raw materials, process conditions, and wastewater segregation practices. It may contain chemicals, hydrocarbons, heavy metals, salts, toxic compounds, refractory organic matter, and high pollutant loads [3], [4], [5], [8].

Table I.1 summarizes the main sources of water pollution and the typical pollutants associated with each source.

Table I.1: *Main sources of water pollution and typical pollutants*

Source category	**Typical origin**	**Common pollutants**	**Main environmental concern**
Domestic wastewater	Households and sanitary facilities	Organic matter, nutrients, suspended solids, microorganisms	Oxygen depletion, eutrophication, microbial contamination
Agricultural runoff	Fertilized soils, livestock areas, irrigation returns	Nitrates, phosphates, pesticides, sediments	Eutrophication, toxicity, sediment transport
Urban runoff	Roads, roofs, parking areas, drainage networks	Hydrocarbons, metals, plastics, suspended solids	Diffuse contamination of surface waters

Industrial wastewater	Refineries and manufacturing industries	Chemicals, hydrocarbons, salts, metals, toxic compounds	High treatment complexity and potential toxicity

I.2.3 Industrial Wastewater as a Specific Pollution Category

Table I.1 shows that industrial wastewater differs from other pollution sources by its complexity, variability, and potential toxicity. Its composition depends on the type of industry, raw materials, production processes, utilities, cleaning operations, and accidental releases. For this reason, industrial wastewater often requires specific characterization and a treatment strategy adapted to the nature of the pollutants present [8].

In petroleum refineries, this specificity is more evident because wastewater may contain conventional pollutants such as COD, BOD_5, TSS, and salts, as well as petroleum-related contaminants such as oil and grease, hydrocarbons, phenols, sulfides, ammonia, and sometimes metals [3], [4], [5]. These pollutants may disturb treatment units, inhibit biological processes, and increase the difficulty of meeting discharge limits.

The management of industrial wastewater is therefore based on two essential principles: reducing pollution at the source and applying an appropriate treatment sequence. Source control includes good housekeeping, leakage prevention, water reuse, and separation of wastewater streams according to their pollution level. Treatment usually combines physical, physico-chemical, biological, and sometimes advanced processes, depending on wastewater quality and final discharge or reuse objectives [5], [7], [8].

I.2.4 Point and Non-Point Pollution Sources

Water pollution sources may also be classified as point sources and non-point sources. Point sources are identifiable and localized discharge points, such as industrial outlets, drainage pipes, or wastewater treatment plant discharges. They are easier to monitor because samples can be collected from a defined location and pollutant concentrations can be measured regularly. Non-point sources are diffuse and originate from large areas, such as agricultural runoff, urban stormwater, or atmospheric deposition.

In industrial environmental management, point-source control is essential because it allows monitoring, regulatory compliance, and treatment before discharge. However, refineries may also be affected by diffuse contamination, especially when rainwater passes through process areas, storage areas, or oily surfaces. For this reason, stormwater management, effluent segregation, and buffer capacity are important elements of refinery wastewater treatment systems [4], [9], [10].

I.3 Wastewater Characteristics and Quality Parameters

I.3.1 Importance of Wastewater Characterization

Wastewater characterization is a fundamental step in wastewater treatment engineering. It provides the basis for understanding the nature of pollution, selecting suitable treatment processes, designing treatment units, and evaluating plant performance. In industrial wastewater treatment, characterization is particularly important because both flow rate and pollutant concentration may vary significantly with production conditions, washing operations, rainfall events, maintenance activities, and accidental releases [3], [4], [5], [8].

The importance of wastewater characterization can be summarized as follows:

I.3.1.1 Identification of pollutant types

Characterization makes it possible to identify the main pollutants present in wastewater, such as suspended solids, hydrocarbons, COD, BOD_5, ammonia, sulfides, phenols, salts, and toxic compounds. This identification helps determine whether the wastewater requires physical, physico-chemical, biological, or advanced treatment [3], [5], [8].

I.3.1.2 Evaluation of pollution strength

Analytical parameters indicate whether the wastewater has low, moderate, or high pollution strength. COD and BOD_5 are used to evaluate organic load, while TSS, oil and grease, ammonia, sulfides, and phenols provide information about specific treatment difficulties [5], [8].

I.3.1.3 Selection of treatment processes

The choice of treatment processes depends directly on wastewater characteristics. High TSS may require sedimentation or filtration, free oil requires oil-water separation, emulsified oil may require coagulation-flocculation and flotation, and biodegradable organic matter requires biological treatment [3], [5], [7], [8].

I.3.1.4 Calculation of pollution loads

Concentration values alone are not sufficient for design or performance evaluation. They must be combined with flow rate to calculate pollution loads. These loads are essential for sizing treatment units and evaluating the real load applied to each process [8].

I.3.1.5 Monitoring of treatment performance

Characterization before and after treatment allows the calculation of removal efficiency and helps identify operational problems. In refinery wastewater treatment, regular monitoring is necessary because sudden variations in oil, COD, TSS, salinity, or toxic compounds can disturb downstream units [4], [7], [8].

I.3.1.6 Support for technical improvement

Reliable analytical data help identify weak points in the treatment chain and support the proposal of technical improvements. In this thesis, wastewater characterization will be used later to interpret refinery data, evaluate treatment performance, and support the proposed modification.

Wastewater quality parameters are generally grouped into physical, chemical, and biological parameters. This classification is developed in the following sections.

I.3.2 Physical Parameters

Physical parameters are often the first indicators used to evaluate wastewater quality. They influence sedimentation, flotation, filtration, oil-water separation, and biological treatment. In refinery wastewater, the most important physical parameters are temperature, suspended solids, turbidity, and oil and grease [3], [5], [8].

I.3.2.1 Temperature

Temperature affects water viscosity, oil droplet rise velocity, dissolved oxygen concentration, and microbial activity. High temperature can reduce oxygen solubility and disturb biological treatment, while low temperature can slow down biodegradation [8].

I.3.2.2 TSS

TSS represents particulate matter retained by filtration. It influences sedimentation, flotation, filtration, sludge production, and final effluent clarity [8].

I.3.2.3 Turbidity

Turbidity expresses the cloudiness of water caused by fine particles, colloids, or emulsified matter. It is useful for assessing the efficiency of clarification, flotation, and filtration [8].

I.3.2.4 Oil and grease

Oil and grease are key indicators in refinery wastewater treatment. They may appear as free oil, dispersed droplets, emulsified oil, or dissolved hydrocarbons. Their presence affects separation, flotation, biological treatment, and final discharge quality, Their monitoring is useful for characterizing oily load, while removal efficiency requires comparable inlet and outlet measurements. [3], [5], [6].

I.3.3 Chemical Parameters

Chemical parameters are used to evaluate the pollution strength and composition of wastewater. They are essential for process control because they influence coagulation efficiency, biological treatment stability, corrosion, toxicity, and discharge compliance [5], [8].

I.3.3.1 pH

pH affects coagulation-flocculation, biological degradation, nitrification, chemical precipitation, corrosion, and discharge compliance [8].

I.3.3.2 COD

COD represents the oxidizable pollution load in wastewater. It is widely used to evaluate the global organic and inorganic oxidizable matter present in the effluent [8].

I.3.3.3 BOD_5

BOD_5 represents the biodegradable organic fraction and is used to estimate the load applied to biological treatment [8].

I.3.3.4 BOD_5/COD ratio

The BOD_5/COD ratio is an indicator of biodegradability. A high ratio generally indicates that a significant part of the organic matter is biodegradable, whereas a low ratio suggests the presence of refractory or toxic compounds. In refinery wastewater, this ratio may vary according to the proportion of biodegradable hydrocarbons, dissolved organics, phenols, sulfides, and inhibitory substances [3], [5], [7].

I.3.3.5 Ammonia, sulfides, and phenols

These compounds are important in refinery wastewater because they may cause toxicity, odor, corrosion, oxygen demand, and biological inhibition. Their monitoring is necessary for evaluating treatment performance and discharge compliance [3], [4], [5].

I.3.3.6 Conductivity and TDS

Conductivity and TDS indicate mineral content and salinity. High salinity can affect biological treatment, limit reuse possibilities, and influence the selection of advanced treatment processes [5], [8].

I.3.4 Biological Parameters and Biodegradability

Biological parameters are important when wastewater is treated using activated sludge, SBR, or other biological processes. The objective of biological treatment is to use microorganisms to convert biodegradable organic matter into biomass, carbon dioxide, water, and stabilized residual products. For this process to be effective, wastewater must contain a biodegradable fraction and must not contain toxic compounds at inhibitory concentrations [7], [8].

In refinery wastewater, biological treatment can reduce BOD_5, biodegradable COD, ammonia, and some dissolved hydrocarbons. However, its performance depends on dissolved oxygen, pH, temperature, hydraulic retention time, organic loading rate, sludge concentration, nutrient balance, and the presence of toxic substances. Excess oil and grease, phenols, sulfides, or shock loads may reduce microbial activity and cause instability in biological reactors [5], [7], [8].

I.3.5 Main Parameters Used in Refinery Wastewater Monitoring

Table I.2 presents the main wastewater quality parameters commonly used in the characterization and monitoring of refinery oily wastewater.

Table I.2: *Main wastewater quality parameters relevant to refinery oily wastewater treatment*

Parameter	Role	Relevance to refinery wastewater treatment
pH	Acidity/alkalinity indicator	Affects coagulation, biological treatment, corrosion, and discharge compliance

Temperature	Thermal condition	Influences oil separation, oxygen transfer, and microbial activity
TSS	Suspended matter	Important for sedimentation, flotation, filtration, and sludge production
Turbidity	Fine particle indicator	Indicates residual suspended and colloidal matter
Oil and grease / hydrocarbons	Oily pollution indicator	Characterizes oily load and supports oil-removal evaluation when paired inlet/outlet data are available.
COD	Oxidizable pollution load	Indicates organic and inorganic oxidizable matter
BOD_5	Biodegradable organic load	Used to evaluate biological treatment load and biodegradability
BOD_5/COD ratio	Biodegradability indicator	Helps assess suitability for biological treatment
Ammonia	Nitrogen compound	Toxic at high concentration and contributes to nitrification oxygen demand
Sulfides	Reduced sulfur compounds	Cause odor, corrosion, toxicity, and oxygen demand
Phenols	Aromatic pollutants	Toxic and may inhibit biological treatment
Conductivity / TDS	Mineral content	Indicates salinity and potential reuse limitations

The parameters listed in Table I.2 show that refinery oily wastewater cannot be evaluated using a single indicator. Physical parameters such as TSS, turbidity, and oil and grease are mainly related to separation, flotation, and filtration efficiency, while chemical and biological parameters such as COD, BOD_5, pH, ammonia, sulfides, phenols, and conductivity are essential for assessing organic load, toxicity, biological treatment suitability, and final discharge compliance.

I.3.6 Pollution Load Calculation

For treatment plant evaluation and design, pollutant concentration alone is not sufficient. A high pollutant concentration at a low flow rate may represent a smaller total load than a moderate concentration at a high flow rate. Therefore, wastewater treatment design uses pollution load calculations that combine concentration and flow rate [8].

The daily pollution load is calculated as:

$$L = Q \times C \qquad \text{(I.1)}$$

where (L) is the pollution load, (Q) is the wastewater flow rate, and (C) is the pollutant concentration. When (Q) is expressed in m^3/day and (C) in mg/L, the load is calculated as:

$$L(Kg/day) = \frac{Q(m^3/day) \times C(mg/L)}{1000} \qquad \text{(I.2)}$$

I.4 Petroleum Refinery Wastewater

I.4.1 Origin of Wastewater in Petroleum Refineries

Petroleum refineries are complex industrial facilities that convert crude oil into valuable products such as fuels, liquefied petroleum gas, naphtha, kerosene, diesel, lubricants, bitumen, and other petroleum fractions. During refining operations, water is used in several direct and indirect applications, including crude oil desalting, steam production, cooling, washing, stripping, equipment cleaning, tank drainage, laboratory activities, and utility systems. These activities generate wastewater streams with different compositions and pollution levels [3], [4], [5].

The origin of refinery wastewater is closely linked to the process units and auxiliary systems operating on site. Desalter effluents may contain salts, oil, suspended solids, and organic compounds removed from crude oil. Sour water and process condensates may contain ammonia, sulfides, phenols, and dissolved hydrocarbons. Oily drainage from process areas, pumps, tanks, and loading zones may contain free and dispersed hydrocarbons. Utility systems may produce blowdown streams rich in dissolved solids and treatment chemicals. Stormwater can also become contaminated when it comes into contact with oily or polluted surfaces [4], [9], [10].

Because of this diversity, refinery wastewater cannot be considered as a single homogeneous effluent. Its quality depends on refinery configuration, crude oil characteristics, operating conditions, maintenance operations, rainfall events, wastewater segregation practices, and accidental releases. Proper identification and separation of wastewater streams are therefore essential for efficient treatment and for reducing the hydraulic and pollutant load applied to downstream units [4], [5], [8].

The generation of refinery wastewater is closely related to the different refining operations and auxiliary processes. Figure I.1 illustrates the main steps of crude oil refining and the associated generation of petroleum refinery wastewater.

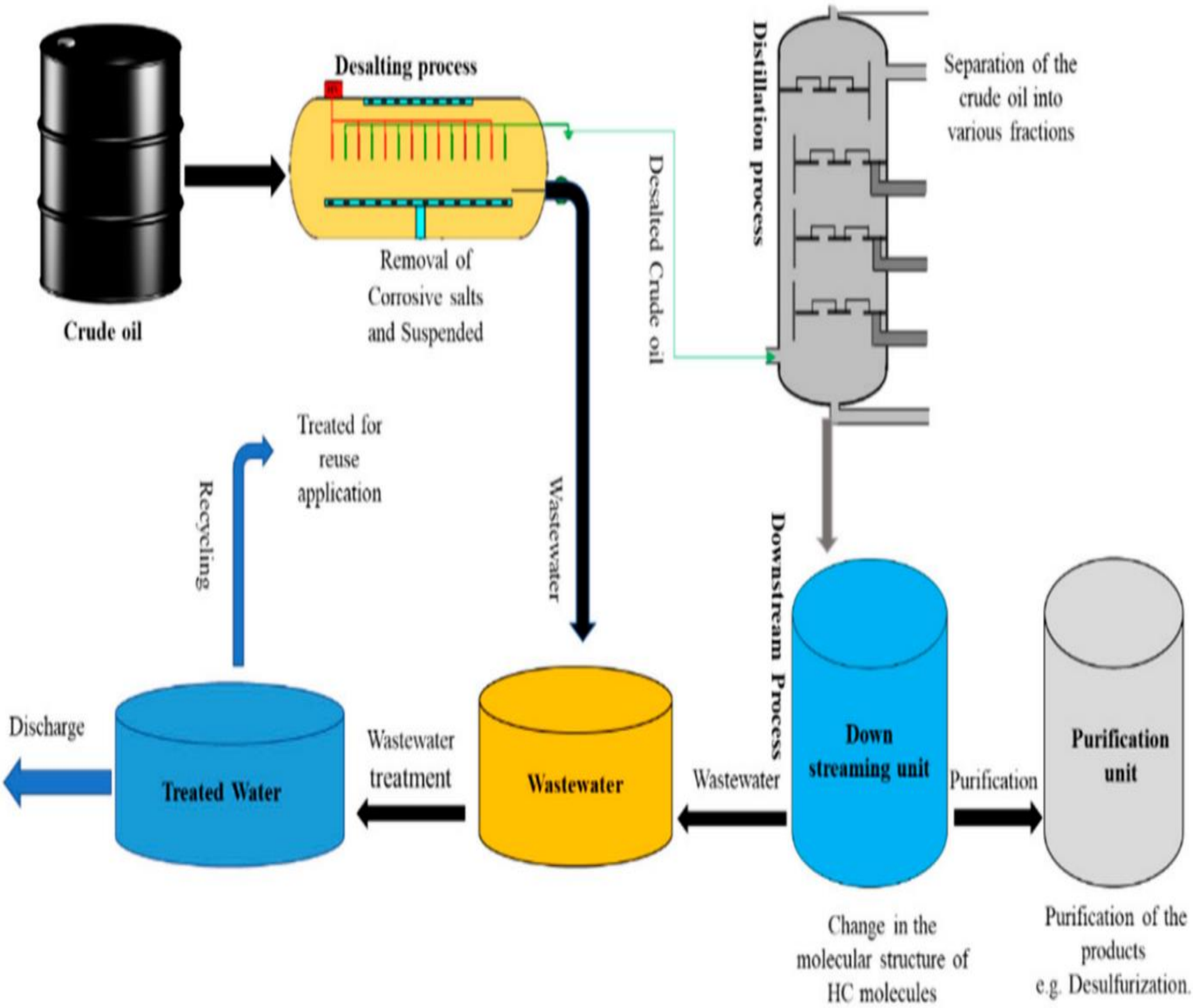


***Figure I.1:** Simplified crude oil refining process and generation of petroleum refinery wastewater, adapted from [5]*

I.4.2 Main Categories of Refinery Wastewater

Refinery wastewater is commonly divided into categories according to its origin and contamination level. This classification is important because each category does not require the same treatment intensity. Less contaminated water should not be mixed unnecessarily with highly polluted streams, because this increases the volume requiring full treatment and may reduce treatment efficiency [4], [8].

The main categories are:

I.4.2.1 Process wastewater

Generated from operations such as desalting, stripping, washing, and process unit drainage.

I.4.2.2 Oily wastewater

Contaminated by free, dispersed, or emulsified hydrocarbons from process areas, tanks, pumps, and oily surfaces.

I.4.2.3 Contaminated stormwater

Rainwater that becomes polluted after contact with process areas, tank farms, roads, or industrial drainage networks.

I.4.2.4 Utility wastewater

Generated from cooling systems, boilers, demineralization units, and other service systems.

I.4.2.5 Sanitary wastewater

Generated by offices, buildings, and sanitary facilities.

I.4.2.6 Accidental contaminated water

Resulting from spills, leaks, firefighting, or emergency drainage [3], [4], [9], [10]

Table I.3 presents the main categories of petroleum refinery wastewater according to their origin, main characteristics, and treatment implications.

Table I.3: *Main categories of petroleum refinery wastewater*

Wastewater category	Typical origin	Main characteristics	Treatment implication

Process wastewater	Desalting, stripping, washing, process units	COD, ammonia, sulfides, phenols, hydrocarbons, salts	Requires controlled collection and complete treatment
Oily wastewater	Process area drainage, pumps, tanks, contaminated surfaces	Free oil, dispersed oil, emulsified oil, TSS	Requires oil-water separation and polishing
Contaminated stormwater	Rainwater from process areas and storage zones	Variable hydrocarbons, solids, sediments	Requires buffering and controlled treatment
Utility wastewater	Cooling systems, boilers, demineralization units	Temperature variation, salts, chemicals	May require separate management depending on quality
Accidental contaminated water	Spills, leaks, firefighting water, emergency drainage	Highly variable, sometimes toxic or concentrated	Requires containment and controlled treatment

.

Table I.3 shows that refinery wastewater is not a single homogeneous effluent. Each category has specific characteristics and treatment requirements. Therefore, proper segregation of wastewater streams is important to avoid unnecessary dilution, reduce the pollutant load applied to treatment units, and improve overall treatment efficiency.

I.4.3 Typical Pollutants in Refinery Wastewater

The composition of refinery wastewater is complex because it contains both conventional wastewater pollutants and petroleum-specific contaminants. Conventional parameters include TSS, COD, BOD_5, pH, nutrients, and dissolved solids. Petroleum-specific pollutants include oil and grease, aliphatic and aromatic hydrocarbons, phenols, sulfides, ammonia, BTEX, PAHs, and sometimes heavy metals [3], [4], [5].

Oil and grease are among the most characteristic pollutants in refinery wastewater. Their presence may result from process leaks, equipment drainage, tank bottom water, contaminated stormwater, or insufficient separation. Suspended solids may come from sediments, corrosion products, process residues, and stormwater runoff. Ammonia and sulfides are often associated with sour water and sulfur-containing petroleum fractions. Phenols may be generated in conversion and cracking processes and are important because of their toxicity and potential inhibition of biological treatment [3], [4], [5].

BTEX and PAHs are of environmental concern due to their toxicity, volatility, persistence, or bioaccumulation potential. Heavy metals may originate from crude oil impurities, catalysts, corrosion products, or process additives. Although their concentrations may vary, their presence must be considered because they can affect sludge quality and biological treatment stability [3], [5], [11].

Figure I.2 presents the major contaminants commonly found in petroleum refinery wastewater.

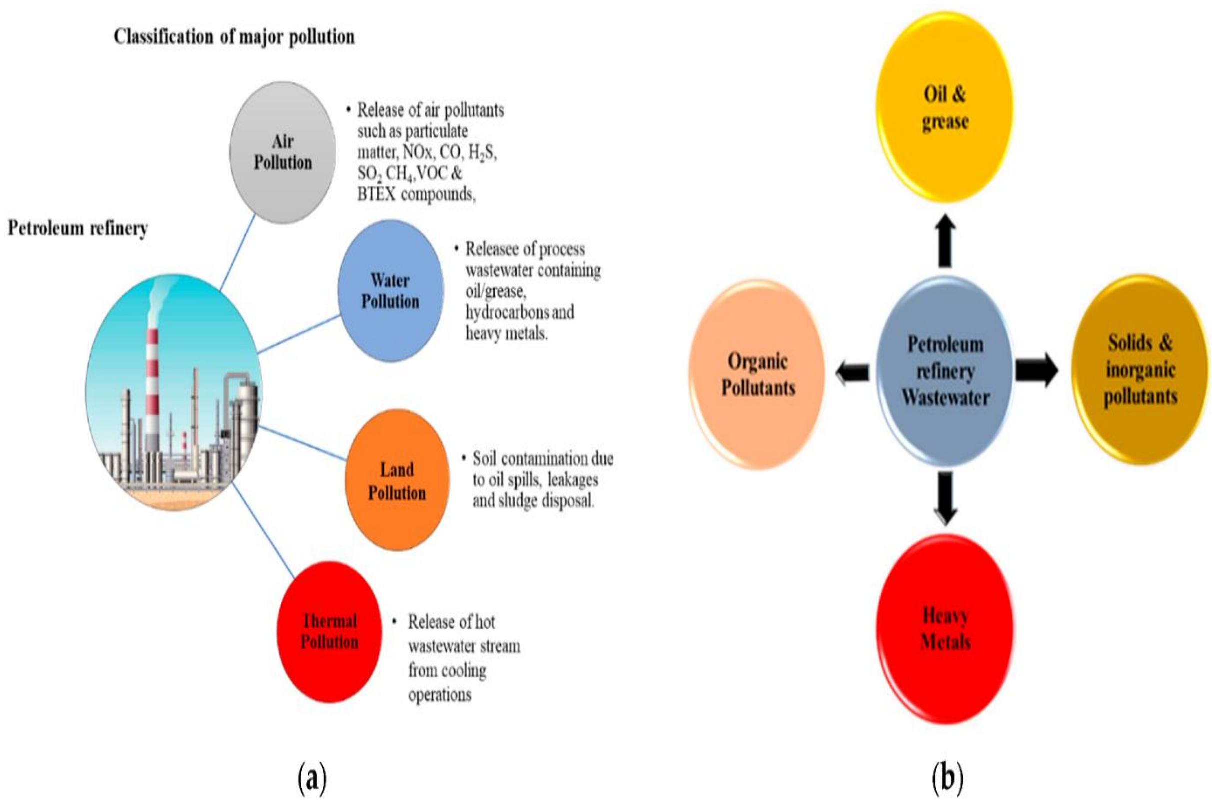


Figure I.2: *Major contaminants found in petroleum refinery wastewater, adapted from [9]*

I.4.4 Variability and Treatment Challenges

One of the main difficulties in refinery wastewater treatment is variability. Flow rate and pollutant concentration may change from one day to another, or even during the same day. This variability may be caused by production changes, unit start-up and shutdown, maintenance activities, tank drainage, cleaning operations, rainfall, accidental leaks, or changes in crude oil quality [4], [7].

Such variations can create hydraulic shocks, organic shocks, oil overloads, salinity fluctuations, or toxic inhibition in treatment units. Excess oil and grease may reduce the efficiency of gravity separators, flotation systems, and biological reactors. High COD loads increase oxygen demand and may disturb biological treatment. High sulfide or phenol concentrations may cause toxicity, odor, corrosion, or microbial inhibition [5], [7], [8].

For these reasons, refinery wastewater treatment requires good monitoring, equalization, process control, and appropriate treatment sequencing. These elements help protect downstream units and improve the stability of the overall treatment system [4], [5], [8].

I.5 Oily Wastewater: Definition and Characteristics

I.5.1 Definition of Oily Wastewater

Oily wastewater is wastewater containing petroleum hydrocarbons, mineral oils, grease, or hydrophobic organic substances in quantities that require specific treatment before discharge or reuse. In petroleum refineries, oily wastewater is mainly generated from process area drainage, equipment washing, pump and valve leaks, tank drainage, floor washing, contaminated stormwater, and accidental hydrocarbon releases [3], [5], [6].

The difficulty of treating oily wastewater is not determined only by the total quantity of oil present, but also by the physical form of oil in water. Hydrocarbons may occur as free oil, dispersed droplets, emulsified oil, or dissolved compounds. Each form has a different separation behavior and requires a different treatment mechanism. This distinction explains why gravity separation alone cannot completely treat refinery oily wastewater [3], [5], [6].

I.5.2 Forms of Oil in Water

Free oil consists of relatively large droplets that rise naturally to the surface because oil is less dense than water. This fraction can generally be removed by gravity separation, skimming, and oil-water separators. Dispersed oil consists of smaller droplets that remain suspended for longer periods and may require coalescence or flotation. Emulsified oil is composed of very fine droplets stabilized by surfactants, fine solids, chemical additives, or natural petroleum compounds. It is more difficult to separate and often requires coagulation-flocculation, flotation, membrane processes, or advanced treatment. Dissolved hydrocarbons are compounds present at the molecular level and cannot be removed by simple physical separation [3], [6], [8].

Table I.4 presents the main forms of oil found in oily wastewater and their implications for treatment process selection.

***Table I.4:** Main forms of oil in oily wastewater and treatment implications*

Form of oil	General description	Separation behavior	Typical treatment approach
Free oil	Large droplets or surface layer	Rises easily by gravity	Skimming, API separation, gravity oil-water separation
Dispersed oil	Small droplets suspended in water	Slow natural separation	Coalescence, flotation, chemical aid
Emulsified oil	Very fine stabilized droplets	Difficult to separate by gravity	Coagulation-flocculation, flotation, membranes
Dissolved hydrocarbons	Hydrocarbon compounds dissolved in water	Not removable by simple separation	Biological treatment, adsorption, oxidation, advanced processes

Table I.4 shows that the treatment difficulty increases when oil passes from free oil to dispersed, emulsified, and dissolved forms. While free oil can generally be removed by gravity separation, emulsified and dissolved fractions require more advanced treatment steps such as coagulation-flocculation, flotation, biological treatment, adsorption, or advanced oxidation processes.

Figure I.3 illustrates the main forms in which oil may be present in oily wastewater.

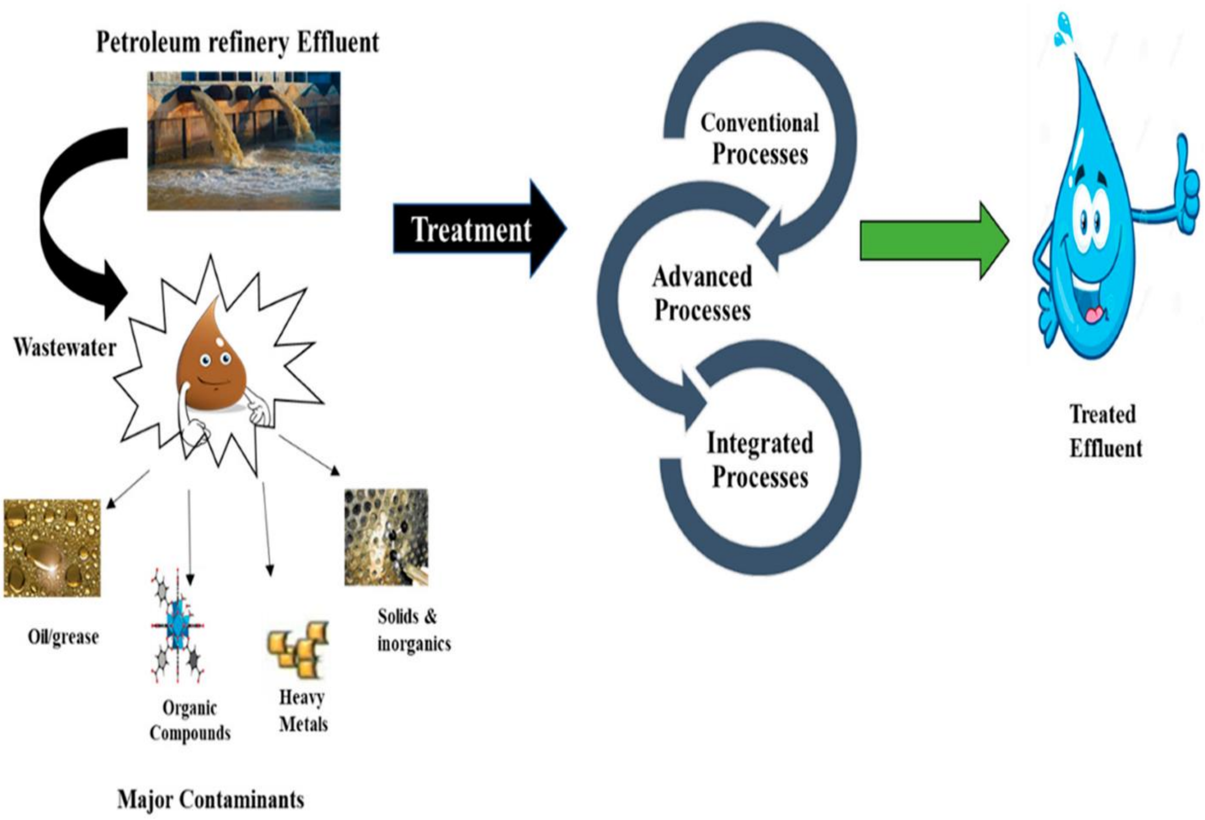


Figure I.3: *Main forms of oil in oily wastewater. Author's own illustration*

I.5.3 Emulsion Stability and Treatment Difficulty

Oil-water emulsions are among the most difficult forms of oily wastewater to treat. Their stability depends on droplet size, surface charge, mixing intensity, natural surfactants, suspended solids, pH, salinity, and chemical additives. In stable emulsions, oil droplets remain finely dispersed and do not easily coalesce or rise to the surface. This reduces the efficiency of gravity separation and increases the need for chemical or enhanced physical treatment [3], [5], [6].

Coagulation-flocculation is commonly used to destabilize emulsified oil and colloidal matter. Coagulation reduces electrostatic repulsion between particles and droplets, while flocculation promotes the formation of larger aggregates. These flocs can then be separated by flotation or sedimentation. In flotation, air or gas bubbles attach to oil droplets, suspended solids, and flocs, carrying them to the surface for removal as scum or sludge [5], [8], [12].

I.5.4 Pollutants Associated with Oily Wastewater

Although oil and grease are the defining pollutants of oily wastewater, refinery oily effluents usually contain a wider range of contaminants. Suspended solids, COD, BOD_5, phenols, sulfides, ammonia, salts, and aromatic hydrocarbons may be present depending on the origin of the wastewater and its mixing with other refinery streams [3], [4], [5].

The interaction between these pollutants influences treatment performance. Suspended solids can stabilize emulsions or increase sludge production. Sulfides and phenols may inhibit biological treatment. High salinity can affect microbial activity and limit reuse possibilities. Dissolved hydrocarbons may contribute to toxicity and residual COD even after oil separation. For this reason, oily wastewater treatment should be evaluated through oil and grease monitoring, oil-removal performance when paired inlet/outlet data are available, and global parameters such as COD, BOD_5, TSS, pH, ammonia, phenols, sulfides, and final effluent quality. [3], [5], [7], [8].

I.6 Environmental and Operational Impacts of Refinery Oily Wastewater

Refinery oily wastewater can affect both the receiving environment and the operation of wastewater treatment systems. Its impacts are not limited to visible oil films; they also include oxygen depletion, toxicity, persistence of hydrocarbons, sludge production, fouling, and inhibition of biological treatment. Therefore, the assessment of oily wastewater must consider environmental impacts and operational constraints at the same time [2], [3], [5], [8].

I.6.1 Environmental Impacts

The environmental impacts of refinery oily wastewater are mainly related to hydrocarbons, organic matter, suspended solids, toxic compounds, and dissolved salts. When oily wastewater is discharged without adequate treatment, it can disturb the natural balance of receiving waters and reduce their ecological and reuse value.

The main environmental impacts include:

I.6.1.1 Reduction of oxygen transfer

Oil films on the water surface reduce contact between air and water. This limits oxygen transfer and can decrease dissolved oxygen availability for aquatic organisms [2], [3], [5].

I.6.1.2 Decrease in light penetration

Floating oil, turbidity, and suspended solids can reduce light penetration into water. This may affect photosynthesis and disturb aquatic ecosystems [2], [8].

I.6.1.3 Oxygen depletion

Organic matter present in refinery wastewater increases oxygen demand during biodegradation. If oxygen consumption becomes higher than natural reaeration, dissolved oxygen decreases and aquatic life may be affected [2], [8].

I.6.1.4 Toxicity to aquatic organisms

Phenols, sulfides, BTEX, PAHs, ammonia, and some metals may cause acute or chronic toxicity depending on concentration and exposure time [2], [3], [5].

I.6.1.5 Persistence and accumulation

Some hydrocarbons, especially PAHs, can persist in sediments and may accumulate in living organisms. This creates long-term environmental risk even when pollution is not immediately visible [5], [11].

I.6.1.6 Limitation of water reuse

High salinity, residual hydrocarbons, suspended solids, and toxic compounds can reduce the suitability of treated water for reuse in industrial or environmental applications [8], [11].

Table I.5 summarizes the main environmental impacts associated with refinery oily wastewater and the pollutants responsible for these effects.

Table I.5: *Main environmental impacts of refinery oily wastewater*

Impact	Main cause	Consequence
Reduced oxygen transfer	Surface oil films	Lower dissolved oxygen availability
Lower light penetration	Oil films, turbidity, suspended solids	Disturbance of photosynthesis and aquatic life
Oxygen depletion	Biodegradable organic matter	Stress on aquatic organisms
Toxicity	Phenols, sulfides, BTEX, PAHs, ammonia, metals	Acute or chronic effects on organisms

Sediment contamination	Persistent hydrocarbons	Long-term pollution risk
Reduced reuse potential	Salinity, residual oil, toxic compounds	Limited industrial or environmental reuse

Table I.5 shows that the environmental impact of refinery oily wastewater is not limited to visible oil pollution. Hydrocarbons, suspended solids, organic matter, sulfides, phenols, ammonia, and salts can affect aquatic ecosystems, reduce oxygen availability, increase toxicity, and limit the safe reuse or discharge of treated effluents. This explains the need for an efficient multi-stage treatment system before final discharge.

I.6.2 Operational Impacts on Treatment Systems

In addition to environmental effects, oily wastewater may create several operational problems inside wastewater treatment plants. These problems are important because they can reduce treatment efficiency, increase operating costs, and affect the reliability of downstream units.

The main operational impacts are:

I.6.2.1 Accumulation of oil and scum

Excess free oil may accumulate in channels, tanks, separators, and basins. This can reduce useful volume, disturb hydraulic flow, and increase cleaning requirements [5], [8].

I.6.2.2 Clogging and fouling

Oil residues and suspended solids can clog pipes, pumps, filters, and distribution systems. Fouling is particularly problematic in filtration and membrane-based processes [5], [8].

I.6.2.3 Increase in sludge production

The removal of oil, grease, suspended solids, and chemical flocs generates sludge that must be thickened, dewatered, treated, or disposed of properly [8].

I.6.2.4 Inhibition of biological treatment

Oil and grease can reduce oxygen transfer and coat biomass surfaces. Toxic compounds such as phenols, sulfides, ammonia, and some aromatic hydrocarbons may inhibit microbial activity and reduce biodegradation efficiency [5], [7], [8].

I.6.2.5 Shock loads and process instability

Sudden increases in flow, oil concentration, COD, salinity, or toxic substances can disturb separation, flotation, and biological treatment. These variations may lead to poor sludge settleability, high oxygen demand, and reduced effluent quality [4], [7], [8].

Therefore, the performance of refinery wastewater treatment depends strongly on the efficiency of upstream treatment stages. Proper segregation, equalization, oil-water separation, coagulation-flocculation, and flotation reduce the load applied to biological treatment and improve process stability [2], [4], [8].

I.6.3 Regulatory Compliance and Water Reuse

Wastewater discharge standards are established to protect receiving environments and limit the impact of industrial effluents. For refinery wastewater, the most important regulated parameters generally include pH, COD, BOD_5, TSS, hydrocarbons, phenols, nitrogen compounds, sulfides, and sometimes metals. Compliance requires a treatment system capable of handling normal operating conditions and occasional variations in flow and pollutant concentration [1], [4], [5].

Beyond regulatory compliance, refinery wastewater treatment is increasingly linked to sustainable water management. Efficient treatment can reduce freshwater consumption, improve internal reuse potential, minimize pollution risk, and support circular economy principles in industrial water use [12]. In this thesis, regulatory and reuse considerations justify the need to evaluate treatment performance using analytical data and to propose realistic technical improvements adapted to refinery operating conditions.

I.7 Overview of Treatment Technologies for Refinery Oily Wastewater

I.7.1 General Treatment Strategy

Refinery oily wastewater treatment is generally based on a multi-stage treatment train. This is necessary because no single process can remove all pollutant forms present in refinery effluents. Free oil, suspended solids, emulsified oil, biodegradable organic matter, ammonia, dissolved hydrocarbons, salts, and refractory compounds each require different removal mechanisms [3], [4], [8].

The general treatment strategy can be summarized as follows:

I.7.1.1 Preliminary treatment

Removes coarse solids, grit, debris, and floating materials to protect pumps, pipes, and downstream equipment.

I.7.1.2 Primary treatment

Removes free oil, grease, and settleable solids using gravity separation, skimming, and sedimentation.

I.7.1.3 Physico-chemical treatment

Removes emulsified oil, colloids, and fine suspended solids using coagulation-flocculation and flotation

I.7.1.4 Biological treatment

Reduces biodegradable COD, BOD_5, and sometimes nitrogen compounds using microbial activity.

I.7.1.5 Tertiary treatment

Improves final effluent clarity and removes residual suspended solids through filtration or polishing processes.

I.7.1.6 Advanced treatment

Targets refractory COD, phenols, residual hydrocarbons, or trace contaminants when conventional treatment is insufficient [3], [5], [7], [8].

Figure I.4 provides a general overview of the main treatment techniques used for petroleum refinery wastewater.

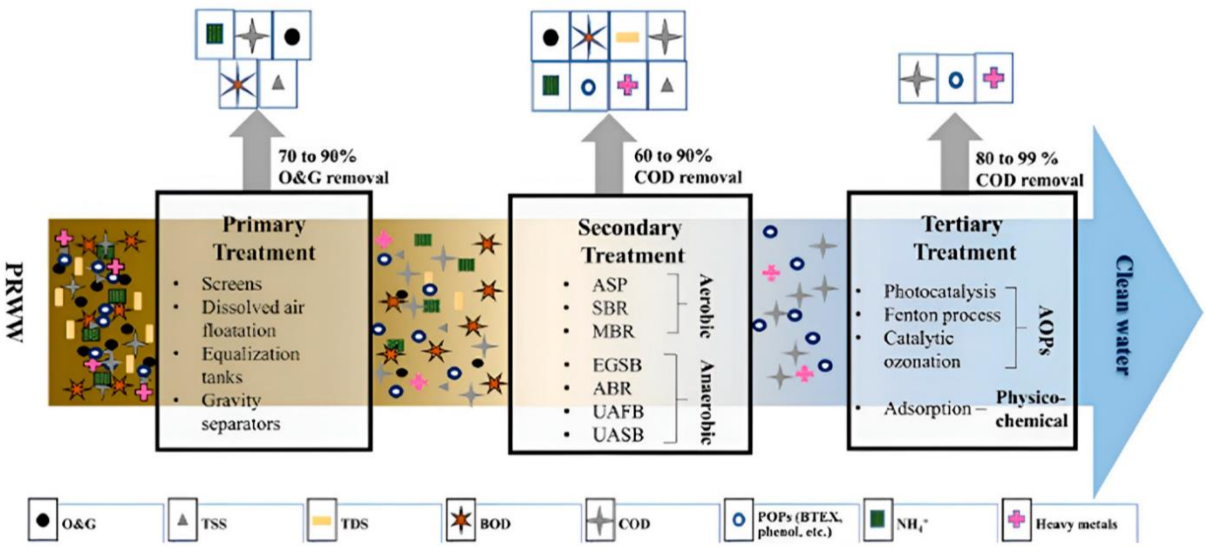


Figure I.4: *General overview of petroleum refinery wastewater treatment techniques, adapted from [9]*

I.7.2 Physical Treatment Processes

Physical treatment processes are based mainly on differences in particle size, density, and phase behavior. They are usually placed at the beginning of the treatment train because they protect downstream equipment and remove pollutants that can be separated without chemical reaction or biological degradation [8].

The main physical processes used in refinery oily wastewater treatment are presented below.

I.7.2.1 Screening

Screening removes coarse solids, debris, and floating materials that may damage pumps, obstruct pipes, or disturb hydraulic flow. It is considered a preliminary treatment step and does not remove dissolved pollutants or emulsified oil [8].

I.7.2.2 Grit removal and sedimentation

Grit removal and sedimentation separate dense particles by gravity. They reduce the accumulation of sand, mineral particles, and settleable solids in basins, separators, pumps, and sludge handling systems [8].

I.7.2.3 Skimming and gravity oil-water separation

Skimming and gravity separation remove free oil and floating hydrocarbons. Oil droplets rise to the surface because oil is less dense than water, while heavier solids settle at the bottom. This process is effective for free oil and large droplets, but it is not sufficient for dispersed, emulsified, or dissolved hydrocarbons [3], [5], [8].

I.7.2.4 Equalization and flow control

Equalization does not remove pollutants directly, but it reduces variations in flow rate and pollutant concentration. It helps limit hydraulic shocks and improves the stability of downstream treatment units [8].

I.7.2.5 Filtration

Filtration removes residual suspended solids and fine particles after upstream treatment. In refinery wastewater treatment, sand filtration is commonly used as a polishing step to improve final effluent clarity before discharge or reuse [5], [8].

Overall, physical treatment is essential as a first barrier in refinery wastewater treatment. However, it has limited efficiency for emulsified oil, colloids, dissolved hydrocarbons, and biodegradable organic matter. Therefore, it is usually followed by physico-chemical and biological processes [3], [5], [8].

I.7.3 Physico-Chemical Treatment Processes

Physico-chemical treatment is used when physical separation alone is not sufficient. This is particularly important for emulsified oil, colloids, and fine suspended solids, which are difficult to remove by gravity separation [3], [5], [8].

The most important physico-chemical processes are:

I.7.3.1 Coagulation

Coagulation destabilizes colloids, fine particles, and emulsified oil droplets by reducing their surface charges. This allows particles and droplets to approach each other and form larger aggregates [5], [8].

I.7.3.2 Flocculation

Flocculation promotes contact between destabilized particles and helps form larger flocs. These flocs can then be removed by flotation, sedimentation, or filtration [8].

I.7.3.3 Flotation

Flotation separates oil droplets, suspended solids, and flocs by attaching them to air or gas bubbles. The formed aggregates rise to the surface and are removed as scum or sludge. DAF and IGF are among the common flotation techniques used for oily wastewater treatment [3], [5], [8], [12].

The efficiency of flotation depends on bubble size, chemical conditioning, hydraulic conditions, oil droplet size, suspended solids concentration, and operating control [5], [8].

I.7.4 Biological Treatment Processes

Biological treatment is used to reduce biodegradable COD, BOD_5, and sometimes nitrogen compounds. It relies on microorganisms that transform organic matter into biomass, carbon dioxide, water, and stabilized products under controlled operating conditions [4], [8].

The main biological processes used in industrial wastewater treatment include:

I.7.4.1 Activated sludge process

The activated sludge process uses suspended biomass under aerated conditions. It is widely applied for the removal of biodegradable organic matter and can be adapted to different industrial effluents when proper pretreatment is provided [8].

I.7.4.2 SBR

The SBR is a fill-and-draw activated sludge system where filling, reaction, settling, decanting, and idle phases occur in the same reactor. This configuration offers operational flexibility and is suitable for variable industrial wastewater when well controlled [7], [8].

I.7.4.3 Biofilm processes

Biofilm systems use microorganisms attached to a support medium. They may provide stable biomass retention and can be useful in some industrial wastewater applications [8].

For refinery wastewater, biological treatment is effective only when the influent is sufficiently pretreated. Excessive oil and grease, toxic compounds, high salinity, or shock loads may inhibit microbial activity and reduce treatment efficiency [5], [7], [8].

I.7.5 Tertiary and Advanced Treatment Processes

Tertiary and advanced treatment processes are applied when additional polishing is required after primary, physico-chemical, and biological treatment. Their use depends on final discharge limits, reuse objectives, and the presence of residual pollutants [5], [8].

The main options include:

I.7.5.1 Sand filtration

Sand filtration removes residual suspended solids, biological flocs, and fine particles. It improves final effluent clarity and protects possible downstream reuse systems [8].

I.7.5.2 Adsorption

Adsorption, especially using activated carbon or other adsorbents, can remove residual organic compounds, phenols, color, odor, and trace hydrocarbons [5], [6].

I.7.5.3 Membrane processes

Membrane processes can produce high-quality effluent by removing fine particles, dissolved compounds, or salts depending on the membrane type. However, fouling and cost are important limitations, especially for oily wastewater [5], [8].

I.7.5.4 AOPs

AOPs are used to degrade refractory organic compounds and residual pollutants through highly reactive oxidizing species. Examples include Fenton, photo-Fenton, ozonation, photocatalysis, and electrochemical oxidation [5], [6].

Table I.6 summarizes the main treatment technologies used for refinery oily wastewater, including their treatment role and main limitations.

Table I.6: *Overview of main treatment technologies for refinery oily wastewater*

	Main processes	**Main role**
Physical treatment	Screening, grit removal, sedimentation, skimming, filtration	Removes coarse solids, settleable matter, free oil, and residual particles
Physico-chemical treatment	Coagulation-flocculation, flotation	Removes emulsified oil, colloids, fine solids, and part of COD
Biological treatment	Activated sludge, SBR, biofilm processes	Reduces biodegradable COD, BOD_5, and nitrogen compounds

Tertiary treatment	Sand filtration and polishing	Improves final effluent clarity and removes residual solids
Advanced treatment	Adsorption, membranes, AOPs	Targets refractory COD, phenols, residual hydrocarbons, and trace pollutants

Table I.6 shows that refinery oily wastewater treatment cannot rely on a single process. Physical treatment is effective for coarse solids and free oil, physico-chemical treatment improves the removal of emulsified oil and fine suspended matter, biological treatment reduces biodegradable organic pollution, and tertiary or advanced processes are used for polishing and residual contaminants. Therefore, an efficient treatment system usually requires a combination of complementary stages.

I.8 Conclusion

This chapter presented the theoretical background required to understand refinery oily wastewater treatment. It introduced water pollution, industrial wastewater, refinery effluents, oily wastewater characteristics, and the main treatment technologies used for this type of effluent.

The main points developed in this chapter can be summarized as follows:

- Industrial wastewater is more variable and complex than domestic wastewater because its composition depends on production processes, raw materials, utilities, cleaning operations, and accidental releases.
- Petroleum refinery wastewater may contain hydrocarbons, suspended solids, organic matter, ammonia, sulfides, phenols, salts, and other pollutants.
- Oily wastewater is difficult to treat because oil may occur as free, dispersed, emulsified, or dissolved fractions.

- Environmental impacts include reduced oxygen transfer, oxygen depletion, toxicity, persistence of hydrocarbons, and reduced water reuse potential.
- Operational impacts include oil accumulation, fouling, sludge production, biological inhibition, and process instability.
- Effective treatment generally requires a multi-stage approach combining physical, physico-chemical, biological, tertiary, and sometimes advanced treatment processes.

These concepts provide the scientific basis for the next chapters. Chapter II will present the industrial site and its wastewater treatment system. Chapter III will use wastewater characterization, regulatory comparison, and engineering calculations to evaluate the existing treatment systems and support the proposed technical improvement.

CHAPTER II

Presentation of Arzew Refinery RA1/Z and Existing Effluent Treatment Systems

CHAPTER II: Presentation of Arzew Rfinery RA1/Z and Existing Effluent Treatment Systems

II.1 Introduction

This chapter presents the industrial context of the study. It is devoted to Arzew Refinery RA1/Z and to the existing effluent treatment systems operating at the refinery, mainly Unit 1800 and Zone 27.

The chapter follows a practical structure. First, it presents the refinery, its historical development, processing capacity, products, and production departments. Then, it introduces the refinery effluent treatment organization and describes the two treatment systems considered in this work. Finally, it presents the main laboratory parameters used to evaluate the quality of industrial effluents.

The objective is not to repeat the general theory of wastewater treatment. The purpose is to describe the real industrial installation, the treatment sequence, and the monitored parameters required to understand the technical study developed in Chapter III.

II.2 Presentation of Arzew Refinery RA1/Z

II.2.1 Historical Background [13]

Arzew Refinery, identified as RA1/Z, is an industrial refining complex operated by Sonatrach in western Algeria. The refinery is located on the El Mohgoun plateau in the Arzew industrial zone, approximately 40 km from Oran. It covers an area of about 170 ha

The refinery was built to process Hassi Messaoud crude oil locally and to supply petroleum products for national needs, particularly fuels for western Algeria, lubricants, and bitumen. Its construction was entrusted to Japan Gasoline Corporation. The first stone was laid on 19 June 1970. The utilities started operation in July 1972, and the refinery units were progressively commissioned until the complete start-up of the complex in March 1973.

After its commissioning, RA1/Z underwent several extensions and modernization works. The main development stages are summarized in Table II.1.

Table II.1: *Main development stages of Arzew Refinery RA1/Z*

Year / Period	Development stage
1970	Beginning of refinery construction.
1972	Start-up of utility units.
1973	Commissioning of the refinery complex.
1975–1977	Extension of bitumen production units.
1978–1984	Development and start-up of an integrated base oil production complex.
1997	Construction of a finished oil packaging unit.
2008 onward	Rehabilitation works to increase crude oil processing capacity and improve product quality.

In addition to its historical development, the geographical location of RA1/Z is important because the refinery is integrated within a larger industrial zone. Figure II.1 shows the location of Arzew Refinery RA1/Z within the Arzew industrial zone and its neighbouring industrial complexes.

Figure II.1 shows the location of Arzew Refinery RA1/Z within the Arzew industrial zone and its neighbouring industrial complexes.

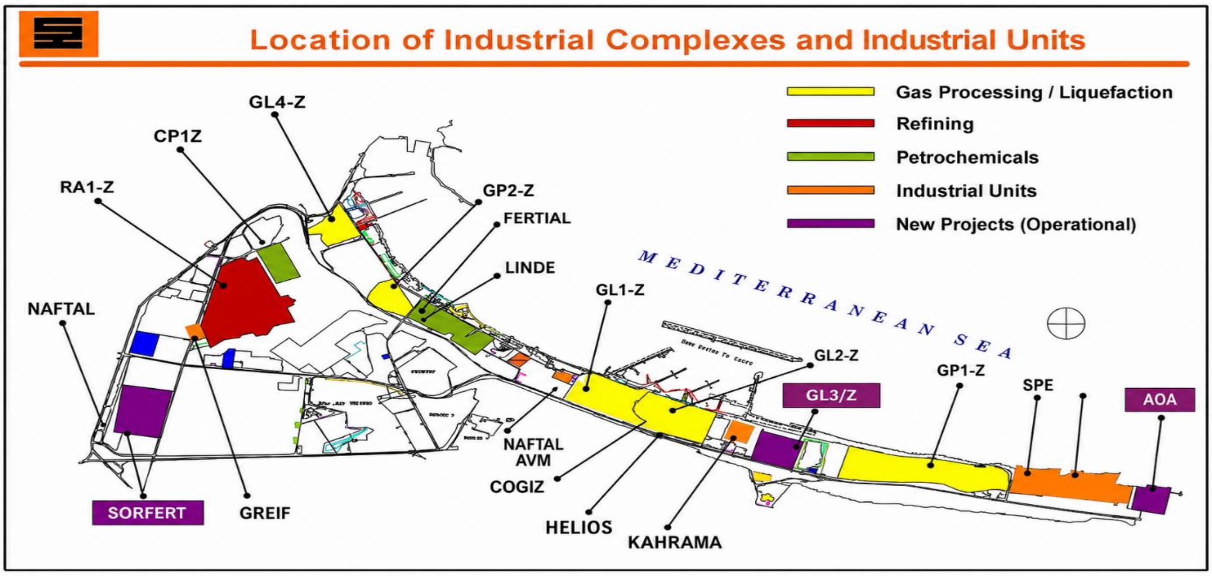


Figure II.1: *Location of Arzew Refinery RA1/Z within the Arzew industrial zone and neighbouring industrial complexes. Adapted from refinery documentation*

II.2.2 Processing Capacity and Main Products

The refinery processes Hassi Messaoud crude oil and reduced crude oil used for bitumen production. According to refinery documentation, the processing capacity is approximately:

- **3.8 million tonnes/year** of Hassi Messaoud crude oil;
- **120,000 tonnes/year** of reduced crude oil for bitumen manufacturing [13].

The main products of RA1/Z are:

- Propane;
- Butane;
- Gasoline;
- Naphtha;
- Kerosene;
- Gas oil;
- Fuel oils;
- Base oils;
- Finished lubricating oils;
- Greases;
- Paraffin;
- Road bitumen;
- Oxidized bitumen.

This production profile explains the presence of several specialized units within the refinery, including fuel production, lubricant production, bitumen production, utilities, storage, dispatching, and effluent treatment facilities.

II.2.3 Production Departments and Main Units

Arzew Refinery RA1/Z includes four production departments. Each department groups several zones and units according to their function. This organization is important because it helps identify the origin of industrial effluents treated later in Unit 1800 and Zone 27.

Figure II.2 presents the general plot plan of Arzew Refinery RA1/Z and shows the distribution of the main zones and units within the refinery.

***Figure II.2**: General plot plan of Arzew Refinery RA1/Z showing the main zones and units. Adapted from refinery documentation.*

II.2.3.1 Production Department P1

Production Department P1 includes the following zones [13]:

Zone 3: Utilities

- Unit 31: steam and electricity production;

- Unit 32: distilled water production;
- Unit 33: cooling water circuit;
- Unit 35: fuel gas system;
- Unit 36: instrument air and service air;
- Unit 37: inert gas production;
- Unit 67: fire-fighting system.

Zone 4: Fuels

- Unit 11: atmospheric distillation;
- Unit 12: reforming;
- Unit 13: gas separation;
- Unit 17: isomerization;
- Unit 18: hot oil system;
- Unit 65: flare gas system.

Zone 7: Lubricants

- Unit 21: vacuum distillation;
- Unit 22: propane deasphalting;
- Unit 23: furfural extraction of aromatics;
- Unit 24: MEK-toluene dewaxing;
- Unit 25: hydrofinishing.

Zone 10: Bitumen

- Unit 14: road bitumen production;
- Unit 15: oxidized bitumen production;
- Unit 45: bitumen loading;
- Unit 49: oxidized bitumen conditioning.

II.2.3.2 Production Department P2

Production Department P2 was developed for base oil production. It includes the following zones [13]:

Zone 19: Utilities

- Unit 1100: steam production;
- Unit 1200: electricity production;

- Unit 1300: cooling tower;
- Unit 1400: fuel gas system;
- Unit 1500: compressed air system;
- Unit 1600: distilled water production;
- Unit 1700: flare system;
- Unit 280: nitrogen production.

Zone 5: Base oils

- Unit 100: vacuum distillation;
- Unit 200: propane deasphalting;
- Unit 300: aromatic extraction;
- Unit 150: hot oil system;
- Unit 160: sour water treatment;
- Unit 400: MEK-toluene dewaxing;
- Unit 500: hydrofinishing;
- Unit 600: paraffin hydrotreatment.

II.2.3.3 Production Department P3

Production Department P3 is mainly dedicated to finished oils, greases, blending, filling, and packaging [13]. It includes:

- Unit 3000: finished oils;
- Unit 3100: oil blending;
- Unit 3200: greases;
- Unit 3300: paraffin conditioning;
- Unit 3600: bulk oil filling;
- Unit 3900: finished oil packaging.

II.2.3.4 Production Department P4

Production Department P4 includes storage, dispatching, and effluent treatment activities [13]. It includes:

Zone 28: Storage and dispatching

- storage of finished petroleum products;
- storage of liquefied petroleum gases;

- storage of additives and blending components;
- storage of Hassi Messaoud crude oil;
- gasoline blending;
- product dispatching by trucks, pipelines, railway, and ships.

Zone 27 and Unit 180 : Effluent treatment

- treatment of refinery industrial effluents;
- separation of hydrocarbons and suspended solids;
- biological treatment where applicable;
- sludge handling and treated water management.

Zone 27 and Unit 1800 are the main wastewater treatment systems considered in this thesis. They are described in detail in Sections II.4 and II.5.

II.3 Presentation of Effluent Treatment at RA1/Z

The refinery generates liquid effluents from process units, utilities, drainage systems, tank areas, washing operations, and rainwater runoff from industrial zones. At RA1/Z, these effluents are not collected in a single stream. They are classified according to their origin and routed through specific sewer networks before treatment [9].

II.3.1 General Classification of Refinery Effluents

The main documented sewer networks used for refinery effluent collection are summarized in Table II.2.

Table II.2: *Main refinery effluent categories at RA1/Z.*

Sewer network	Effluent category	Main origin
Sewer No. 25	Clear water	Rainwater from roofs, roads, and clean areas.
Sewer No. 26	Oily or loaded water	Drainage from process areas, pumps, equipment, tanks, and oily industrial zones.
Sewer No. 27	Process wastewater	Polluted process streams, including condensates and solvent-related operations.

Sewer No. 28	High-salinity water	Cooling water blowdown, boiler blowdown, demineralization regeneration effluents, and saline streams.

This classification is important because each sewer network may present different hydraulic and pollution characteristics. Oily water, process wastewater, and high-salinity water do not require the same treatment constraints. Therefore, effluent separation at the collection stage helps organize the downstream treatment process.

II.3.2 Existing Effluent Treatment Facilities

At RA1/Z, the effluent treatment systems considered in this study are Unit 1800 and Zone 27:

- **Unit 1800:** treatment of refinery effluents collected from sewer networks No. 25, 26, 27, and 28 [9].
- **Zone 27:** treatment of drainage effluents originating from the production units of Department P1 [10].

The following sections present each system separately according to its influent origin, treatment sequence, main equipment, and treated water/sludge management. Calculations, pollutant load evaluation, treatment performance, and technical modification proposals are developed in Chapter III.

II.4 Description of Unit 1800 [9]

Unit 1800 is one of the existing effluent treatment facilities at RA1/Z. It is designed to treat mixed refinery wastewater collected from different sewer networks before discharge or possible reuse. The treatment line includes successive physical, physico-chemical, biological, and filtration steps.

II.4.1 Role and Influent Origin

The role of Unit 1800 is to treat effluents originating mainly from the refinery sewer networks listed below:

- **Sewer No. 25:** clear water;
- **Sewer No. 26:** oily or loaded water;

- **Sewer No. 27:** process wastewater;
- **Sewer No. 28:** high-salinity water.

The influent is therefore a mixed industrial stream. Its characteristics depend on the contribution of each sewer network and on operating conditions within the refinery.

Table II.3 presents the main influent characteristics of Unit 1800, including the design flow rate and the principal pollution parameters considered in the treatment process.

Table II.3: *Main influent characteristics of Unit 1800.*

Parameter	**Value / indication**
Maximum treatment flowrate	About 83 m^3/h
Rain peak flowrate	Up to about 1300 m^3/h
Flow type	Continuous flow with rainy episodes
Main origin	Clear water, oily water, process wastewater, high-salinity water, purges, and stormwater runoff
Hydrocarbons	Up to about 500 ppm
Specific compounds	Possible traces of furfural, MEK, toluene, phenols, H_2S, NH_3, and naphthenic acids
Salinity	High, mainly related to Sewer No. 28
Main operating constraint	High hydraulic variability

II.4.2 Treatment Process of Unit 1800

The treatment process of Unit 1800 is arranged as a sequence of unit operations. Each step prepares the effluent for the next one by removing a specific fraction of the pollution load.

Figure II.3 presents the simplified treatment line of Unit 1800, showing the main water, oil, and sludge treatment paths.

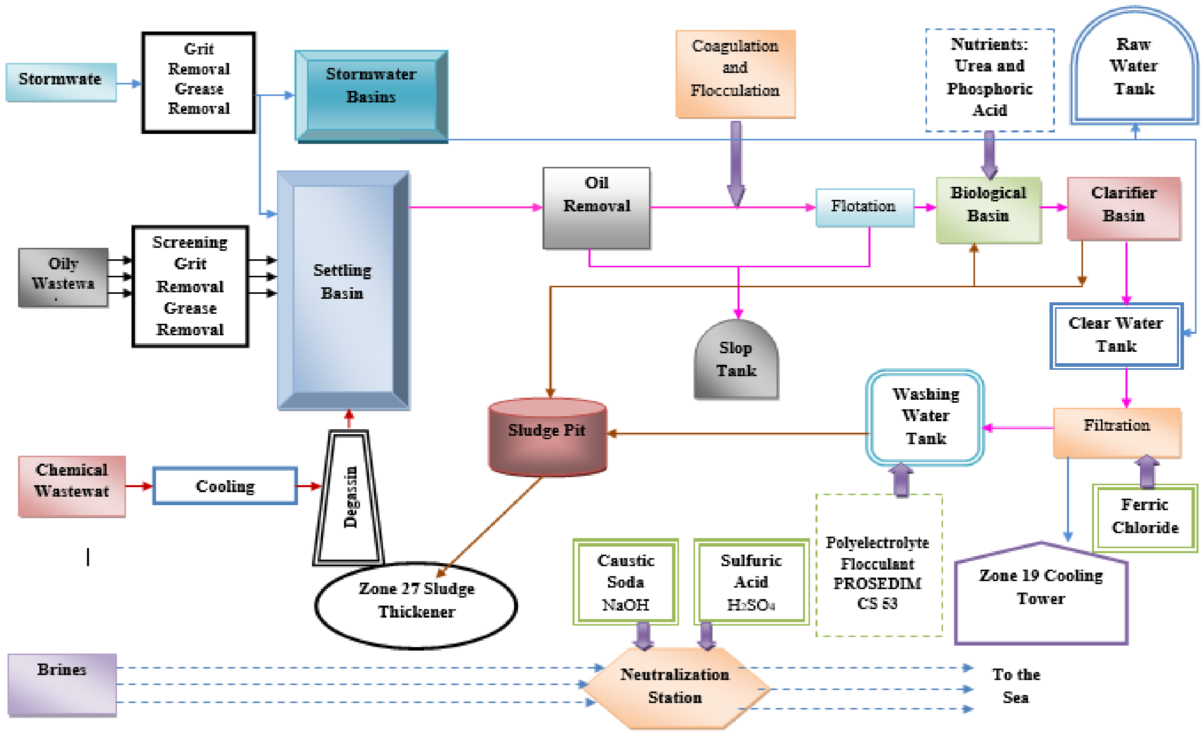


***Figure II.3**: Simplified treatment line of Unit 1800. Adapted from internal refinery process diagram.*

Figure II.3 shows that Unit 1800 treatment is organized as a sequence of complementary stages, including preliminary treatment, oil-water separation, physico-chemical treatment, biological treatment, filtration, and sludge handling.

Table II.4 summarizes the treatment sequence of Unit 1800 and indicates the main role of each treatment stage.

***Table II.4:** Treatment sequence of Unit 1800.*

Step	Main units / operations	Main function
Preliminary treatment	Screening, grit removal, grease removal, cooling, degassing	Protection of downstream units and preparation of wastewater for treatment.
Primary treatment	API separator	Removal of free hydrocarbons and settleable solids by gravity separation

Physico-chemical treatment	Coagulation–flocculation and flotation	Removal of emulsified oil, fine suspended solids, and flocs.
Secondary treatment	Biological basin and clarifier	Reduction of biodegradable organic matter and separation of biological sludge.
Tertiary treatment	Sand filtration	Final removal of residual suspended solids.
Sludge treatment	Sludge collection, sludge thickener, and sludge dewatering	Concentration, volume reduction, and handling of sludge produced during treatment.

II.4.3 Main Equipment and Process Transition

The treatment line of Unit 1800 can be described according to the transition between the main process stages.

II.4.3.1 Preliminary treatment

The influent first passes through preliminary treatment. This part removes coarse solids, sand, and floating grease in order to protect pumps, pipes, and downstream equipment. The main equipment includes screening, grit removal, and grease removal systems.

Figure II.4 shows the grit and grease removal section used in the preliminary treatment of Unit 1800.

Figure II.4: *Grit and Grease Removal*

II.4.3.2 Cooling and degassing section

After preliminary treatment, the effluent passes through cooling and degassing. Cooling lowers the wastewater temperature to conditions more suitable for downstream treatment. Degassing removes gases and light hydrocarbon traces that may affect safety and process stability.

Figure II.5 shows the cooling and degassing section of Unit 1800, which is used before the downstream oil-water separation and treatment stages.

Figure II.5: *Cooling and degassing section of Unit 1800*

II.4.3.3 API separation

The effluent then enters the API separator. This equipment operates by gravity separation. Free hydrocarbons rise to the surface, while settleable solids move toward the bottom. The separated oil and sludge are collected separately.

Figure II.6 shows the API basins used in Unit 1800 for the gravity separation of free oil and settleable solids from the incoming oily wastewater.

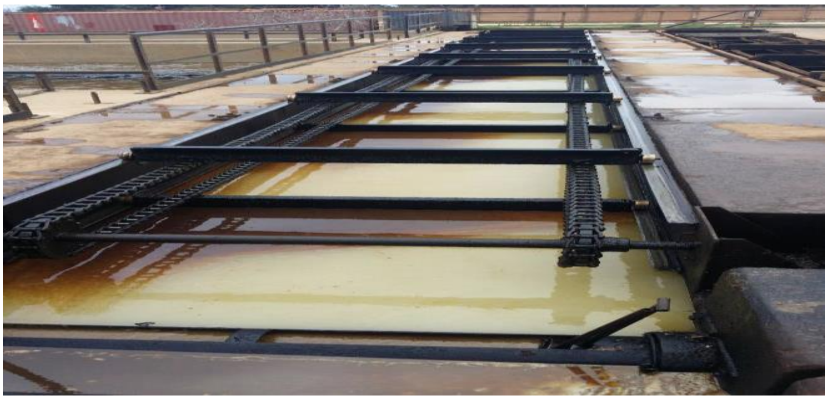


Figure II.6: *API Basins*

II.4.3.4 Coagulation–flocculation and flotation

After API separation, residual fine particles and emulsified oil may remain in the water. Coagulation–flocculation is used to form flocs that can be separated more easily. The effluent then passes to flotation, where air bubbles attach to oil droplets and flocs, causing them to rise to the surface for removal.
Figure II.7 shows the flotation unit of Unit 1800, which is used to improve the removal of fine suspended matter and residual oily pollutants after the upstream separation stages.

Figure II.7: Flotation unit

Figure II.8 shows the air supply system of Unit 1800, which supports aeration and air distribution within the treatment process.

Figure II.8: *air supply system of Unit 1800*

II.4.3.5 Biological treatment and clarification

After flotation, the effluent is directed to the biological treatment section. This stage is based on activated sludge and is used to reduce biodegradable organic matter. Aeration and mixing maintain the biomass in suspension and provide oxygen required for biological oxidation.

The effluent then passes to the clarifier. The role of the clarifier is to separate the biological sludge from the treated water. Settled sludge is either returned to maintain the biological process or extracted as excess sludge according to the operating conditions.

Figure II.9 shows the biological treatment basin of Unit 1800, where biodegradable organic matter is reduced under controlled aeration conditions.

Figure II.9: *Biological treatment basin of Unit 1800*

II.4.3.6 Sand filtration

The final polishing step is sand filtration. It removes residual suspended solids that remain after biological treatment and clarification. The filtered water is then directed toward the treated water outlet or reuse line according to the operating configuration.

Figure II.10 shows the sand filtration system of Unit 1800, which is used as a final polishing step to improve treated water quality.

Figure II.10: *Sand filtration system of Unit 1800*

II.4.4 Sludge and Treated Water Management

The solids extracted from Unit 1800 come mainly from API separation, flotation, and biological clarification.

The handling line includes:

- collection from the different treatment units;
- transfer to the thickener;
- dewatering of the thickened material;
- final handling or transfer according to the operating procedure [10].

The thickener increases the solids concentration and reduces the volume sent to dewatering. The dewatering unit then lowers the water content further, which facilitates transport, disposal, or transfer to the appropriate management system.

Figure II.11 shows the sludge thickener of Unit 1800, which is used to increase sludge concentration before dewatering.

Figure II.11: *Sludge thickener of Unit 1800*

Figure II.12 shows the sludge dewatering unit of Unit 1800, which is used to reduce the water content of thickened sludge before final handling or transfer.

Figure II.12: *Sludge dewatering unit of Unit 1800.*

II.5 Description of Zone 27 [10]

Zone 27 is an effluent treatment facility of RA1/Z designed for the treatment of industrial wastewater before final discharge. The treatment system includes water treatment, sludge treatment, and incineration/flue gas treatment sections.

The water treatment line is based on the following main sequence:

- pretreatment and stormwater management;
- API separation;
- IGF/EGF flotation;
- SBR biological treatment;
- sand filtration;
- sludge extraction and treatment.

Figure II.13 presents the technological scheme of the Zone 27 wastewater treatment system, showing the main water, oil, and sludge treatment circuits.

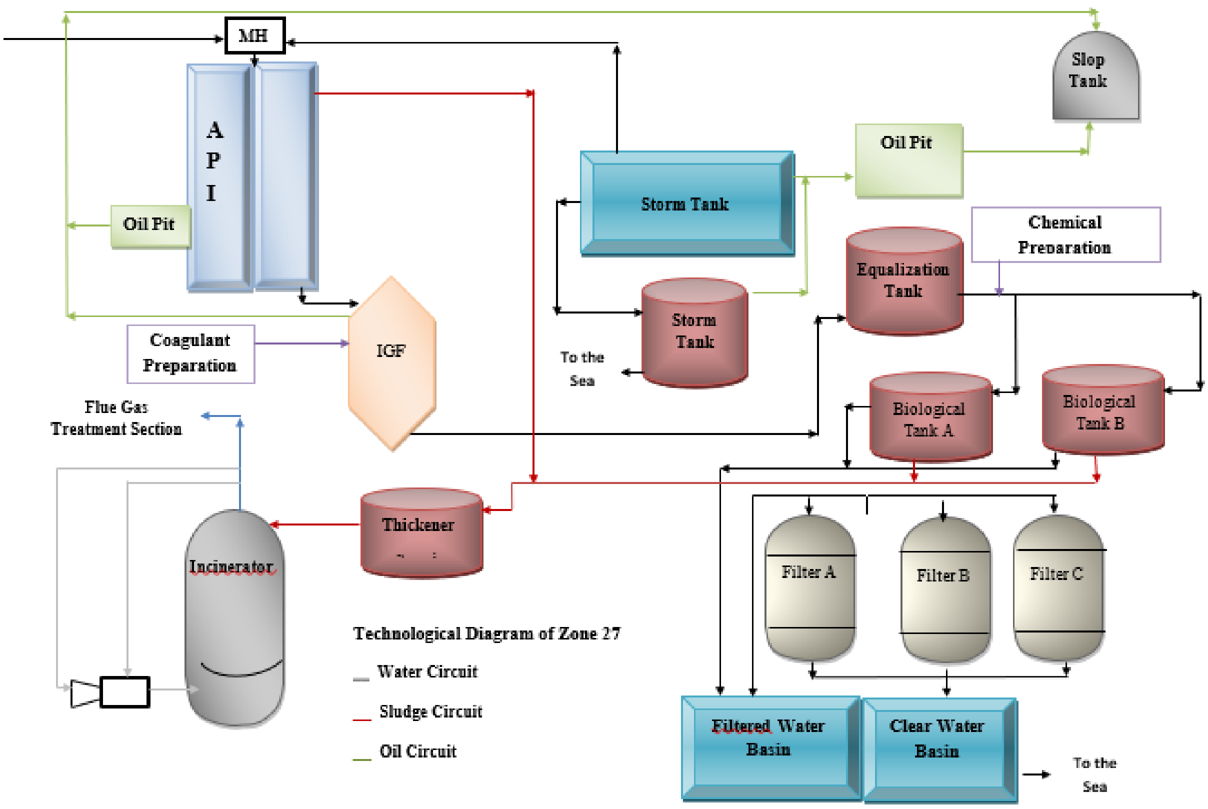


Figure II.13: *Technological scheme of Zone 27 wastewater treatment system. Adapted from internal refinery process diagram*

II.5.1 Role and Influent Origin

Zone 27 receives industrial effluents requiring a complete treatment line for the removal of hydrocarbons, suspended solids, and biodegradable organic pollution. The system is also designed to manage hydraulic variations caused by stormwater events.

The main influent characteristics considered for Zone 27 are summarized in Table II.5.

Table II.5: *Main influent characteristics of Zone 27*

Parameter	Value / indication
Normal flowrate	150 m^3/h, including 10 m^3/h return from 27-T01
Design flowrate	200 m^3/h
Rain flowrate	3300 m^3/h
Hydrocarbons and grease	5000 ppm
Suspended solids	400 ppm
Soluble COD	550 ppm
BOD_5	83 ppm
NH_3	72 ppm
H_2S	< 15 ppm
Furfural	1 ppm
MEK	1 ppm
pH	5.5–8.5
Temperature	10–35°C

II.5.2 Pretreatment and Stormwater Management

The pretreatment section is used to receive the incoming wastewater and manage high hydraulic flows during rainy periods. It includes stormwater routing, preliminary solids removal, oil recovery, and transfer toward the treatment line.

The stormwater basin is divided into functional zones:

- **pre-sedimentation zone:** removal of coarse solids and settled matter;
- **pre-deoiling zone:** recovery of free hydrocarbons from the surface;

- **pumping zone:** transfer of the wastewater toward the buffer tank and downstream treatment.

During normal operation, wastewater is directed toward the API separation system. During high rainfall events, excess flow can be temporarily stored in the stormwater basin before being treated progressively.

Figure II.14 shows the stormwater basin of Zone 27, which is used for temporary collection and management of stormwater before controlled treatment.

Figure II.14: *Stormwater basin of Zone 27*

II.5.3 API Separation

After pretreatment, wastewater is directed to the API separator. The API unit provides primary separation based on density differences between water, free hydrocarbons, and settleable solids.

The main functions of the API separator are:

- separation of free hydrocarbons at the water surface;
- settling of heavy suspended solids;
- reduction of the hydrocarbon load before flotation;
- transfer of separated oil and sludge to their respective collection systems.

Figure II.15 shows the API separator of Zone 27, which is used for the gravity separation of free hydrocarbons and settleable solids from oily wastewater.

Figure II.15: *Zone 27 API Separator*

II.5.4 IGF/EGF Flotation

The effluent from the API separator is sent to the flotation system. In Zone 27, the flotation step is used to remove residual free hydrocarbons and suspended solids after primary separation.

The system operates with chemical conditioning and air dispersion. Aluminum sulfate is used as coagulant to promote the formation of separable flocs. Air bubbles generated in the flotation cells attach to oil droplets and flocs, allowing their rise to the surface and removal by skimming.

The flotation section includes:

- coagulant preparation and dosing system;
- flotation cells;
- aeration or air dispersion system;
- surface skimming system;
- sludge/slop collection system.

According to the operating documentation, the flotation system is designed for inlet free hydrocarbons below 300 ppm and suspended solids below 100 ppm, with high removal efficiency for free hydrocarbons and suspended matter.

Figure II.16 shows the IGF/EGF flotation unit of Zone 27, which is used to remove residual free hydrocarbons, fine suspended solids, and oily particles after API separation.

Figure II.16: *IGF/EGF flotation unit of Zone 27*

II.5.5 SBR Biological Treatment

After flotation, the wastewater is transferred to the biological treatment section. Zone 27 uses SBR reactors based on the activated sludge process. The objective of this stage is to reduce biodegradable organic matter under controlled aeration, mixing, settling, and decantation conditions.

The SBR operating principle is based on sequential phases carried out in the same reactor:

- filling;
- reaction/aeration;
- settling;
- decantation;
- excess sludge withdrawal when required.

This configuration allows biological treatment and clarification to occur in the same tank. The treated supernatant is then transferred toward the tertiary filtration step.

Figure II.17 shows the SBR biological reactor of Zone 27, where biological treatment is carried out through successive operating phases.

Figure II.17: *SBR biological reactor of Zone 27*

Figure II.18 illustrates the main operating phases of the SBR biological treatment process used in Zone 27.

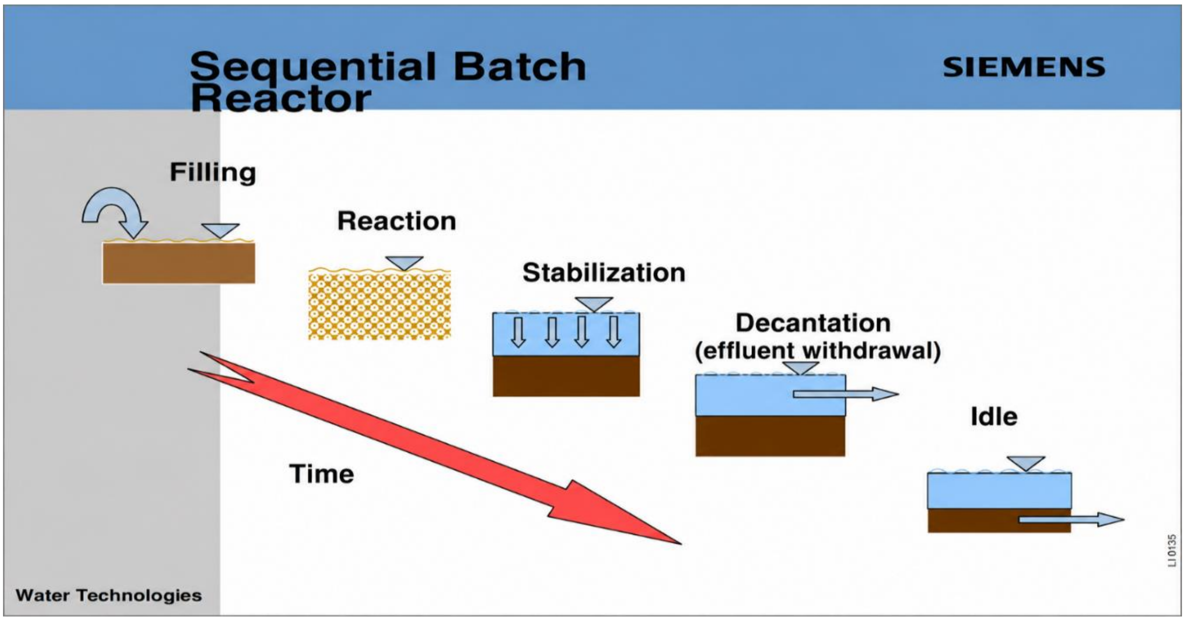


Figure II.18: *Biological SBR Treatment Phases*

II.5.6 Sand Filtration and Sludge Management

The tertiary treatment step consists of sand filtration. Its role is to remove residual suspended solids after biological treatment and improve the quality of treated water before discharge

The sand filtration section includes several filters operating according to the treatment demand. Filter backwashing is carried out when required to restore filtration efficiency.

Figure II.19 shows the sand filters of Zone 27, which are used as a polishing step before final treated water discharge or management.

Figure II.19: *Sand filters of Zone 27*

Sludge is generated from the API separator, flotation system, and biological treatment. The sludge line includes collection, transfer, thickening, and downstream handling. Zone 27 also includes sludge treatment and incineration/flue gas treatment sections according to the operating documentation.

Figure II.20 shows the sludge thickener of Zone 27, which is used to concentrate sludge before the downstream sludge treatment and final handling steps.

Figure II.20: *Sludge thickening or sludge handling section of Zone 27*

Zone 27 also includes a sludge incineration section. The incinerator is used for the thermal treatment of the produced sludge after the required conditioning steps. The incineration line is associated with a flue gas treatment section, which is included in the Zone 27 operating documentation

Figure II.21 shows the sludge incinerator of Zone 27, which is used for the final thermal treatment of sludge generated by the wastewater treatment process.

Figure II.21: *Sludge incinerator of Zone 27*

II.6 Laboratory Monitoring Parameters for Refinery Effluents

The quality of refinery effluents at RA1/Z is monitored through laboratory analysis bulletins. These bulletins report the analytical parameters used to follow the quality of industrial effluents and support operational control.

In this section, only the parameters appearing in the refinery analysis bulletins are presented. The analytical procedures are based on internal laboratory methods and standards used by the refinery laboratory [14].

II.6.1 Physical and General Parameters

The physical and general monitoring parameters include:

- **Temperature**, measured when required to evaluate operating conditions;
- **pH at 25°C**, used to control acidity or alkalinity;
- **Conductivity**, used as an indicator of dissolved salts and mineralization;
- **Dissolved oxygen**, used mainly for biological treatment control.

These parameters are important for following the operating conditions of the treatment line, especially in units where biological treatment and salinity variations may affect performance.

II.6.2 Organic and Oily Pollution Parameters

The main parameters related to organic and oily pollution are:

- **Hydrocarbons**, used to characterize oily pollution and, when paired inlet and outlet measurements are available, to evaluate oil removal efficiency;
- **COD**, used to estimate chemically oxidizable pollution;
- **BOD_5**, used to estimate biodegradable organic pollution;
- **Phenol content**, used to monitor phenolic contamination when present.

These parameters are directly related to the performance of API separation, flotation, biological treatment, and final effluent quality.

II.6.3 Suspended and Nutrient-Related Parameters

The bulletins also include parameters related to suspended matter and nutrients:

- **Suspended solids**, used to evaluate particulate pollution;
- **Total Kjeldahl nitrogen**, used to monitor nitrogen compounds;
- **Phosphates**, used to monitor phosphorus concentration.

These parameters are useful for assessing clarification, flotation, filtration, and the nutrient balance required for biological treatment.

II.6.4 Specific Refinery Compounds and Inorganic Parameters

Some parameters are specific to refinery operations or to potential process-related contamination. The analysis bulletins include:

- **Furfural** is monitored because it is related to solvent-bearing process streams and may affect biological treatment if present at significant concentrations.
- **MEK**;
- **H_2S**;
- **Iron**;
- **Lead**.

Their presence in the monitoring program is related to refinery process activities, solvent use, corrosion products, sulfide-containing streams, or trace inorganic contamination.

Table II.6 summarizes the main parameters appearing in the refinery effluent analysis bulletins and used for the monitoring of treated wastewater quality.

Table II.6: *Main parameters appearing in refinery effluent analysis bulletins.*

Group	Parameters
Physical and general parameters	Temperature, pH, conductivity, dissolved oxygen
Organic and oily pollution	Hydrocarbons, COD, BOD_5, phenol content
Suspended and nutrient-related parameters	Suspended solids, total Kjeldahl nitrogen, phosphates
Specific refinery and inorganic parameters	Furfural, MEK, H_2S, iron, lead

Table II.6 shows that the monitoring of refinery effluents is based on general, organic, oily, nutrient-related, and specific refinery parameters. These parameters provide the analytical basis for the evaluation of effluent quality and treatment performance in the following chapter.

II.7 Conclusion

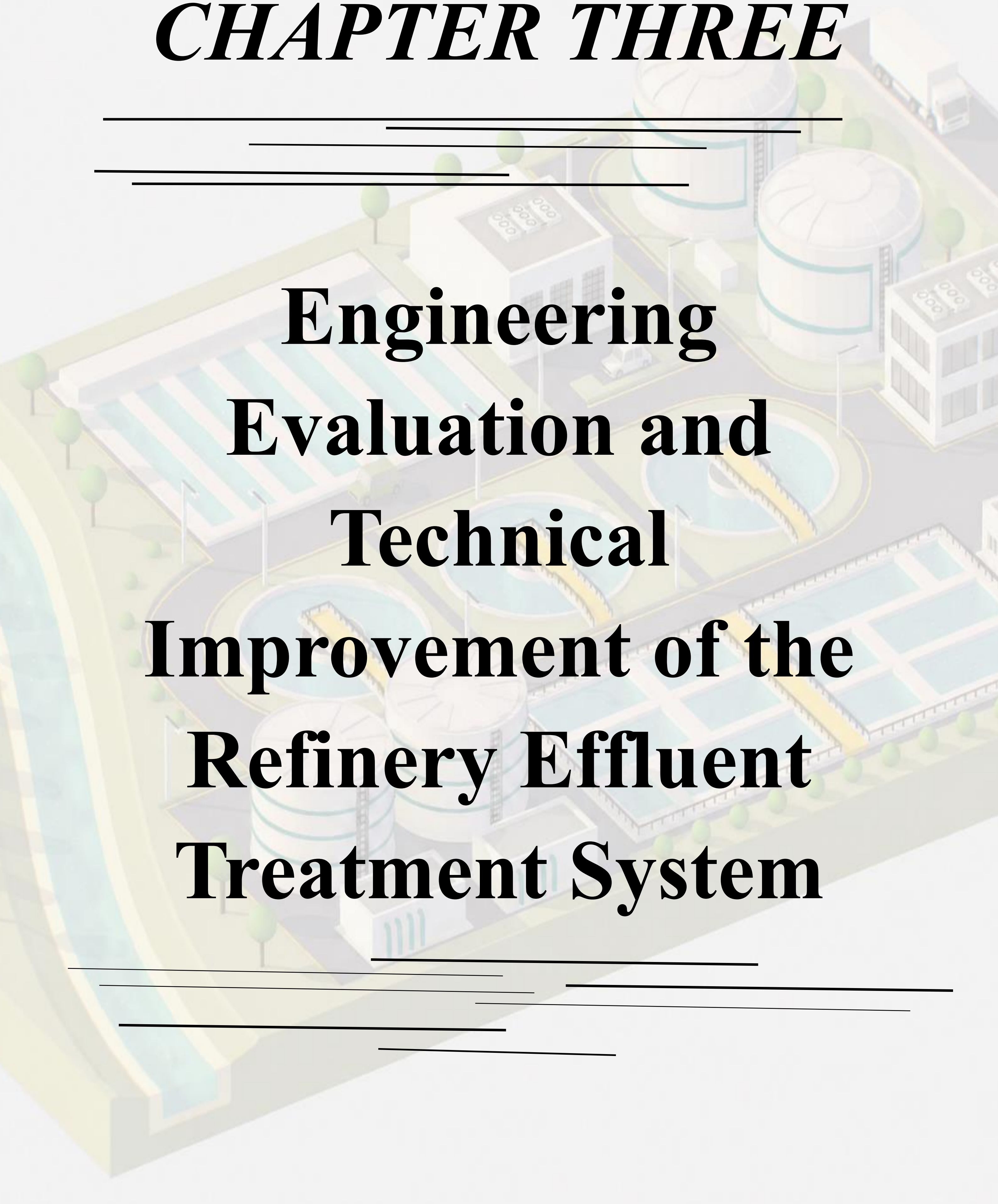
This chapter presented the industrial context of the study. Arzew Refinery RA1/Z was described through its historical development, processing capacity, main products, and production departments. The organization of the refinery shows the presence of several process, utility, storage, dispatching, and effluent treatment areas.

The chapter also presented the refinery effluent collection system and the two wastewater treatment facilities considered in this thesis: Unit 1800 and Zone 27. Unit 1800 treats mixed effluents collected from several refinery sewer networks, while Zone 27 includes a treatment line based on pretreatment, API separation, IGF/EGF flotation, SBR biological treatment, sand filtration, and sludge management.

The monitored parameters used by the refinery laboratory were also introduced, including pH, temperature, suspended solids, conductivity, hydrocarbons, COD, BOD_5, total Kjeldahl nitrogen, phosphates, furfural, and MEK. These parameters will be used in the following chapter for the analysis of effluent quality, treatment performance, pollutant loads, and the development of the proposed technical modification.

CHAPTER THREE

Engineering Evaluation and Technical Improvement of the Refinery Effluent Treatment System



CHAPTER III: Engineering Evaluation and Technical Improvement of the Refinery Effluent Treatment System

III.1 Introduction

This chapter presents the applied engineering evaluation of the refinery effluent treatment systems studied in this work. It focuses on Unit 1800 and Zone 27, which are two existing treatment stations at Arzew Refinery RA1/Z. The objective is to use real laboratory monitoring data, operating information, and regulatory references to evaluate the quality of the treated effluents and identify the main operational limitations affecting treatment stability.

The chapter is based on the operating manuals of Unit 1800 and Zone 27 [9], [10], general wastewater treatment engineering principles [8], Algerian regulatory limits for industrial liquid effluent discharges [15], and the internal laboratory results organized for the selected monitoring period. Scientific interpretation is supported by petroleum refinery wastewater treatment literature [3], [7], [5].

The analysis is not limited to describing the existing treatment units. It aims to connect measured data with engineering interpretation. For this reason, the chapter distinguishes between inlet characterization parameters and outlet quality parameters. Particular attention is given not only to furfural peaks at the inlet, but also to the outlet organic quality represented by COD and BOD_5, because these parameters directly reflect the remaining oxidizable and biodegradable pollution after treatment. The chapter also compares the treated effluent with the applicable regulatory limits, interprets the biodegradability of the wastewater, and identifies the technical problem that justifies the proposed improvement.

III.2 Methodological Approach

The methodology adopted in this chapter is designed to evaluate the performance of two existing refinery effluent treatment systems using a selected monthly dataset. The work follows a progressive logic: first, the monitoring data are organized; second, the inlet and outlet parameters are interpreted separately; third, the outlet results are compared with regulatory limits; fourth, the main treatment limitation is identified; and finally, a technical solution is selected and preliminarily sized.

The adopted methodology includes the following steps:

- selection of a common monitoring period for Unit 1800 and Zone 27;
- organization of laboratory data into inlet and outlet parameters;
- identification of valid measurements and exclusion of blank cells from calculations;
- statistical analysis of the main measured parameters;
- comparison of outlet quality with Algerian regulatory limits;
- interpretation of the BOD5/COD ratio as a biodegradability indicator;
- identification of the main operational limitation from the data;
- proposal and preliminary sizing of a technical solution adapted to the identified limitation.

III.3 Selected Study Period and Data Organization

III.3.1 Selected Monitoring Period

The selected monitoring period extends from **15 April 2026 to 14 May 2026**. This period was selected because it provides a common one-month dataset for both Unit 1800 and Zone 27, allowing the two stations to be evaluated over the same time window.

The selected dataset includes the old effluent treatment station, Unit 1800, and the new effluent treatment station, Zone 27. This distinction is important because Unit 1800 and Zone 27 are not evaluated using the same regulatory reference. Unit 1800 is considered an old installation, whereas Zone 27 is considered a new installation.

III.3.2 Inlet and Outlet Monitoring Logic

The laboratory monitoring structure must be interpreted carefully. For both Unit 1800 and Zone 27, hydrocarbons and furfural are mainly measured at the inlet. These parameters are used to characterize the incoming oily and solvent-related load.

At the outlet, the monitoring focuses on treated effluent quality parameters such as pH, conductivity, COD, BOD_5, TSS, phenol, H2S, iron, lead, and other parameters when available. These outlet parameters are used to evaluate the quality of the treated effluent and its compliance with regulatory references.

It is important to note that the inlet hydrocarbon load does not mean that the whole free-oil load reaches biological treatment. Before the downstream treatment stages, free oil is separated by gravity decantation and recovered as slop, while the water phase continues through the treatment line. Therefore, hydrocarbons at the inlet mainly indicate the severity of the incoming oily load, while the risk for biological treatment is more related to residual emulsified oil, dissolved organic compounds, furfural, and soluble COD/BOD_5 that may remain in the water phase.

III.3.3 Importance and Risk of Furfural

In this study, furfural is considered an important solvent-related parameter because it may create inhibitory conditions for biological treatment when present at high concentrations. However, the evaluation is not limited to furfural alone. COD and BOD_5 are also essential parameters because they represent the oxidizable and biodegradable organic load remaining in the effluent. Therefore, furfural is interpreted together with COD, BOD_5, and the BOD_5/COD ratio in order to understand both inlet shock events and outlet treatment performance.

III.3.4 Regulatory Basis for Effluent Evaluation

The regulatory comparison is based on Executive Decree No. 06-141 of 19 April 2006, which defines the limit values for industrial liquid effluent discharges in Algeria [15]. For this study, the distinction between old and new installations is essential.

Unit 1800 is treated as an old installation and is compared with the tolerance values for old installations. Zone 27 is treated as a new installation and is compared with the limit values for new installations.

For direct comparison with laboratory results expressed in mg/L, the general limit values of Annex I are used when the units are compatible. The petroleum refining-specific table in the same decree is relevant to the sector, but some of its parameters are expressed in g/t. Therefore, these values should not be directly compared with laboratory concentrations in mg/L unless the necessary conversion basis is available.

Table III.1 presents the regulatory reference values used in this study for the direct comparison with laboratory results.

Table III.1: Regulatory reference values used for direct comparison with laboratory results

Parameter	**Unit**	**Zone 27: new installation limit**	**Unit 1800: old installation tolerance**
pH	-	6.5-8.5	6.5-8.5
Temperature	°C	30	30
MES/TSS	mg/L	35	40
Kjeldahl nitrogen	mg/L	30	40
Total phosphorus	mg/L	10	15
COD	mg/L	120	130
BOD_5	mg/L	35	40
Phenol index	mg/L	0.3	0.5
Total hydrocarbons	mg/L	10	15
Oils and grease	mg/L	20	30
Lead	mg/L	0.5	0.75
Iron	mg/L	3	5

The regulatory values shown above are used for direct comparison with the monthly laboratory results when the units are compatible.

III.4 Calculation Methods

III.4.1 Descriptive Statistics

For each measured parameter, the following values are calculated: number of valid measurements, minimum, maximum, average, and standard deviation. These indicators help identify stable parameters, abnormal values, and peak events.

III.4.2 Pollution Load

Pollution load is calculated when both concentration and flow rate are available:

$$L = \frac{Q \times C}{1000} \qquad \text{(III.1)}$$

where L is the pollutant load in kg/day, Q is the flow rate in m^3/day, and C is the concentration in mg/L.

III.4.3 Removal Efficiency

Removal efficiency is calculated only when paired inlet and outlet concentrations are available for the same parameter and comparable sampling period:

$$Removal\ efficiency\ \eta\ (\%) = \frac{Cin - Cout}{Cin} \times 100 \qquad \text{(III.2)}$$

In this chapter, removal efficiency is not calculated for hydrocarbons and furfural because these parameters are mainly measured at the inlet in the selected dataset.

III.4.4 Biodegradability Ratio

The BOD_5/COD ratio is calculated as:

$$BOD_5/COD\ ratio = BOD_5 / COD$$

This ratio is not a regulatory value. It is used only as a technical indicator of biodegradability and biological treatment suitability. COD and BOD_5 are compared separately with the regulatory limits.

III.5 Inlet Characterization of Unit 1800 and Zone 27

III.5.1 Inlet Hydrocarbon Load

Figure (III.1) shows the variation of inlet hydrocarbon concentration versus time for Unit 1800 and Zone 27 during the selected period.

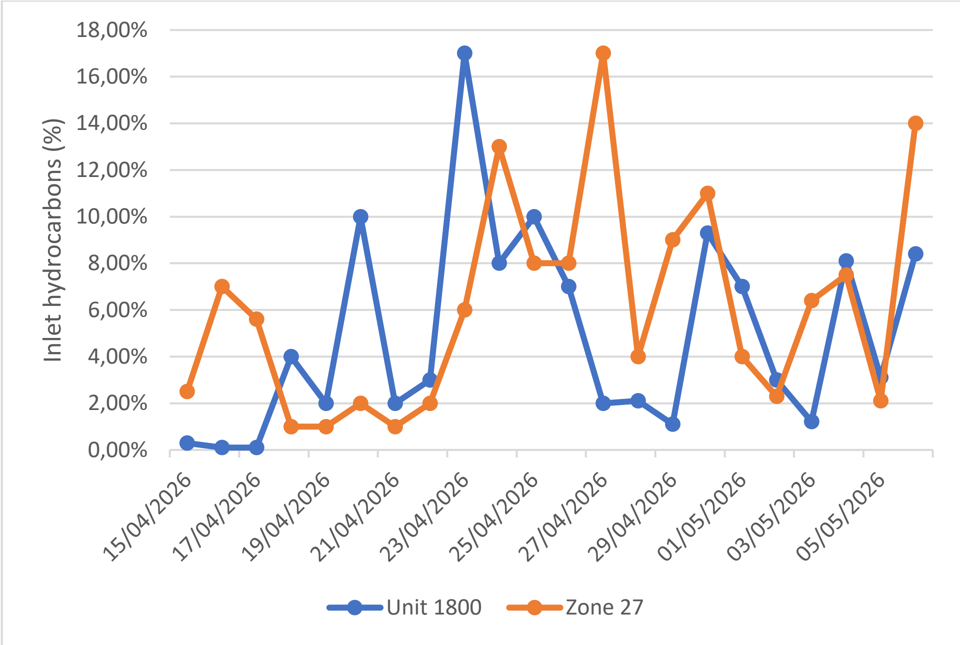


Figure III.1: *Variation of inlet hydrocarbons in Unit 1800 and Zone 27 during the selected period*

Figure III.1 shows significant fluctuations in inlet hydrocarbon concentration for both Unit 1800 and Zone 27. These variations indicate that the oily wastewater entering the treatment systems is not constant and may be affected by refinery operating conditions, drainage events, and wastewater segregation. The presence of several peaks confirms the importance of preliminary oil removal and hydraulic control before downstream treatment stages.

III.5.2 Inlet Furfural Load

Furfural measured at the inlet is used as an indicator of solvent-related process discharge. Its variation is important because it may reveal the arrival of specific process wastewater that can affect biological treatment if it remains in the water phase.

Figure (III.2) shows the variation of inlet furfural concentration versus time for Unit 1800 and Zone 27 during the selected period.

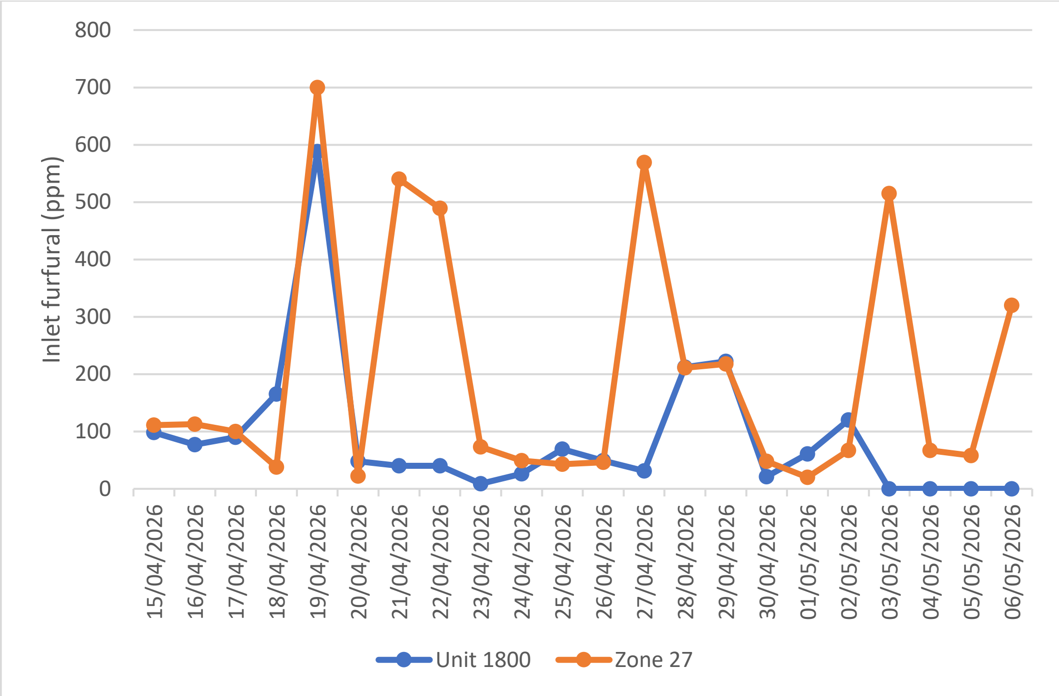


Figure III.2: *Variation of inlet furfural in Unit 1800 and Zone 27 during the selected period*

Figure III.2 shows that inlet furfural concentration varied considerably during the selected period. Zone 27 recorded several high peaks, while Unit 1800 showed fewer and lower peaks, with one major increase around 19/04/2026. These fluctuations indicate that furfural enters the treatment systems irregularly and may create shock conditions for the biological treatment stage. Since furfural can negatively affect microbial activity, its presence must be controlled before the effluent reaches the biological reactors.

Table III.2 summarizes the influent characterization of Unit 1800 and Zone 27 during the selected period.

Table III.2: *Summary of influent characterization during the selected period*

Station	Parameter	Number of measurements	Minimum	Maximum	Average	Standard deviation	Interpretation

Unit 1800	Inlet hydrocarbons	22	0.10%	17.00%	4.95%	4.36%	Highly variable oily load
Unit 1800	Inlet furfural	22	0.00 ppm	588.00 ppm	89.37 ppm	128.75 ppm	Solvent-related peaks observed
Zone 27	Inlet hydrocarbons	22	1.00%	17.00%	6.11%	4.55%	Highly variable oily load
Zone 27	Inlet furfural	22	20.00 ppm	700.00 ppm	200.78 ppm	216.14 ppm	Stronger solvent-related variability

The influent characterization shows that both stations receive variable oily and solvent-related wastewater. Zone 27 shows a higher average inlet furfural concentration than Unit 1800, which indicates stronger solvent-related variability during the selected period.

III.6 Outlet Quality Evaluation

III.6.1 Outlet Hydrocarbon

Figure (III.3) Variation of outlet HC concentration (mg/L) versus time for Unit 1800 and Zone 27 compared with the regulatory limit values and the performances of the new and old installations.

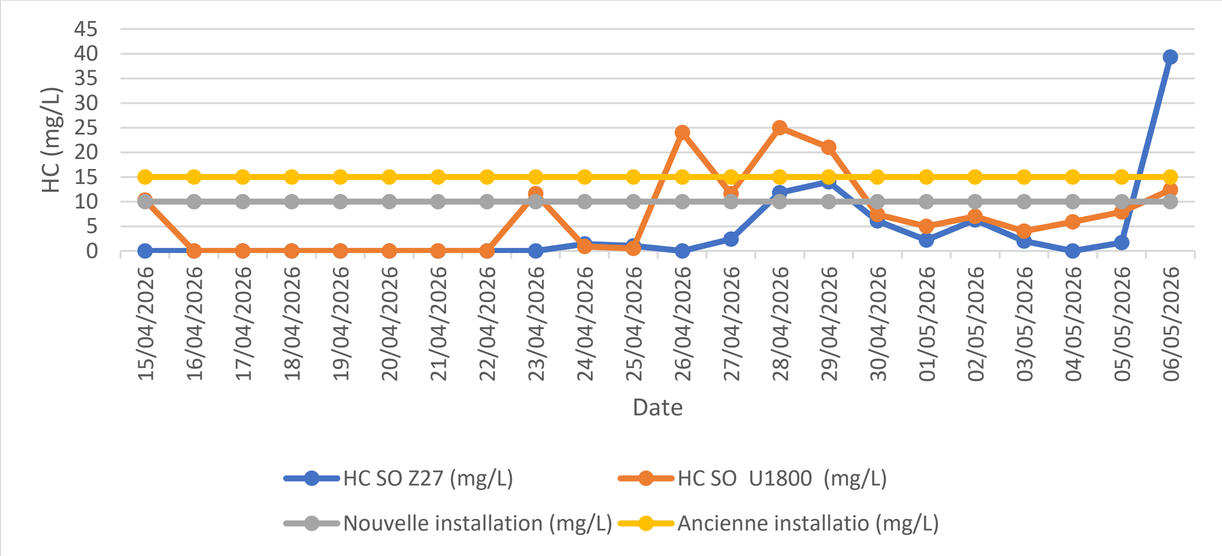


Figure III.3 Outlet HC variation compared with regulatory limits

The temporal evolution of HC concentration indicates variations in the treatment performance during the monitoring period. Overall, the new installation showed a more consistent behavior than the old installation, maintaining HC concentrations closer to the regulatory requirements. These results suggest an improvement in the operational efficiency of the treatment system, despite the occurrence of occasional fluctuations

III.6.2 Outlet pH

Outlet pH indicates the general stability of the treated effluent and its compatibility with discharge requirements. For both stations, the relevant pH range is 6.5-8.5.

Figure (III.4) shows the variation of outlet pH versus time for Unit 1800 and Zone 27 compared with the lower and upper regulatory limits.

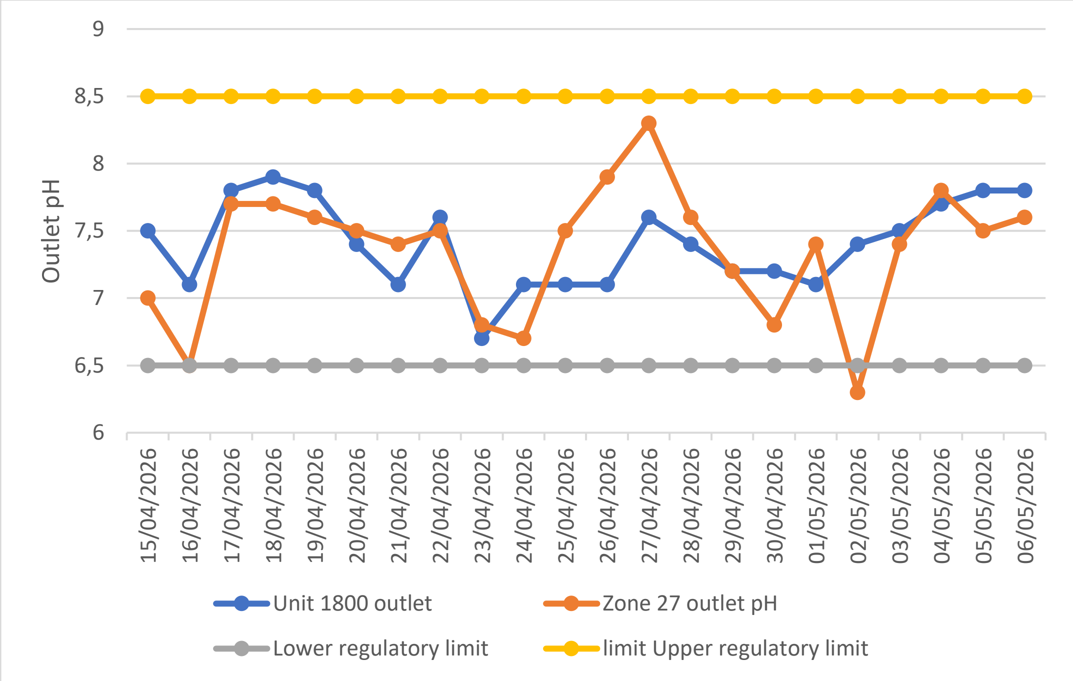


Figure III.4: *Outlet pH variation compared with regulatory limits*

Figure III.4 shows that the outlet pH values of Unit 1800 and Zone 27 were generally within the regulatory range of 6.5 to 8.5 during the selected period. Unit 1800 showed relatively stable values, mostly between neutral and slightly alkaline conditions. Zone 27 also remained within the acceptable range in most measurements, although one value was slightly below the lower limit. Overall, pH does not appear to represent the main treatment limitation, but its continuous monitoring remains necessary because pH stability is important for biological treatment performance and final discharge compliance.

III.6.3 Outlet COD

COD is one of the most important indicators of organic pollution in refinery effluent. It must be compared with the correct regulatory reference: the old-installation tolerance for Unit 1800 and the new-installation limit for Zone 27.

Figure (III.5) shows the variation of outlet COD concentration versus time for Unit 1800 and Zone 27 compared with the regulatory limits.

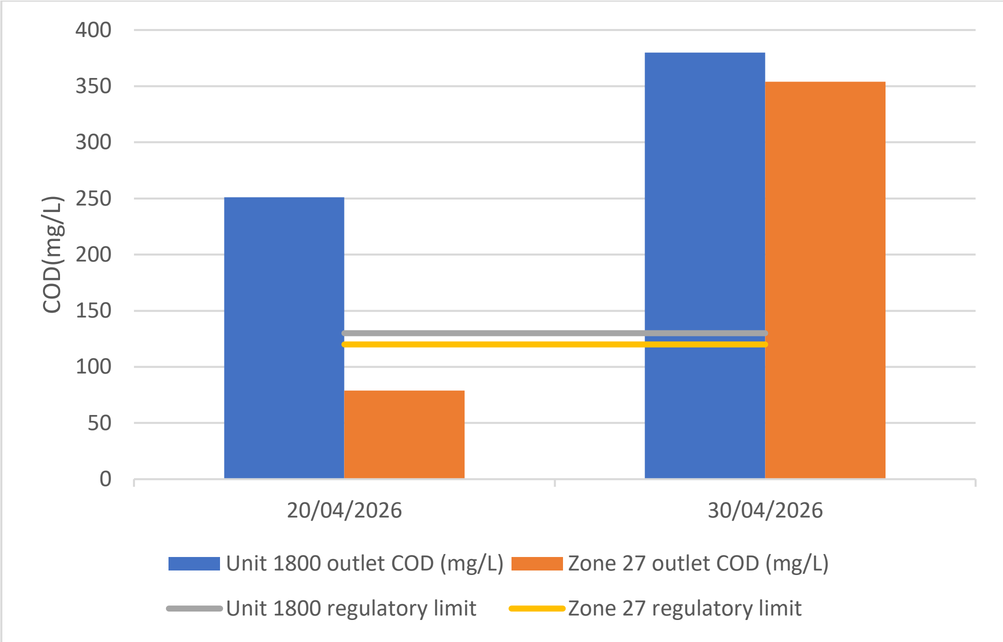


Figure III.5: *Outlet COD measurements compared with regulatory limits*

Figure III.5 shows that the outlet COD values exceeded the regulatory limits in most measurements during the selected period. Unit 1800 recorded high COD concentrations on both dates, while Zone 27 showed a compliant value on 20/04/2026 followed by a significant exceedance on 30/04/2026. These results indicate the presence of residual oxidizable organic pollution in the treated effluent and show that COD represents an important treatment limitation during the selected monitoring period.

III.6.4 Outlet BOD_5

BOD_5 reflects the biodegradable part of the organic load. High BOD_5 values at the outlet may indicate organic shock loads or reduced biological treatment efficiency.

Figure (III.6) shows the variation of outlet BOD_5 concentration versus time for Unit 1800 and Zone 27 compared with the regulatory limits.

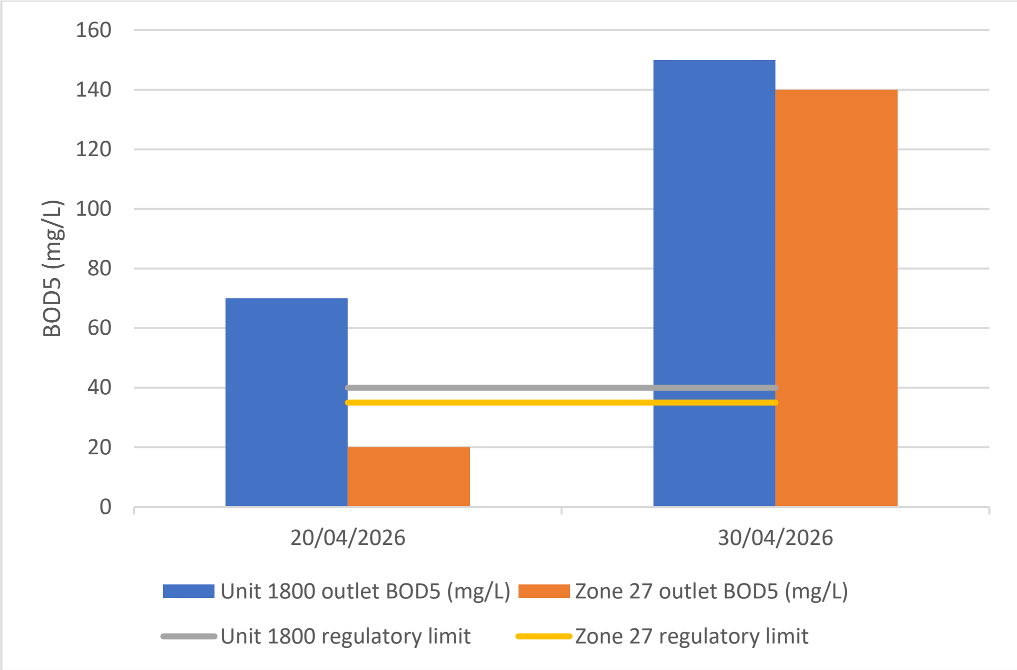


Figure III.6: *Outlet BOD5 measurements compared with regulatory limits*

Figure III.6 shows that the outlet BOD_5 values exceeded the regulatory limits in most measurements during the selected period. Unit 1800 exceeded the limit on both dates, while Zone 27 showed a compliant value on 20/04/2026 but a high exceedance on 30/04/2026. These results indicate that biodegradable organic matter was not sufficiently reduced during some monitoring days, which confirms the need to protect and stabilize the biological treatment stage.

III.6.5 Outlet TSS

MES evaluates the removal of suspended solids. If TSS remains low while COD and BOD_5 are high, the main limitation is more likely related to dissolved or biodegradable organic pollution rather than suspended solids.

Figure (III.7) shows the variation of outlet TSS concentration versus time for Unit 1800 and Zone 27 compared with the regulatory limits.

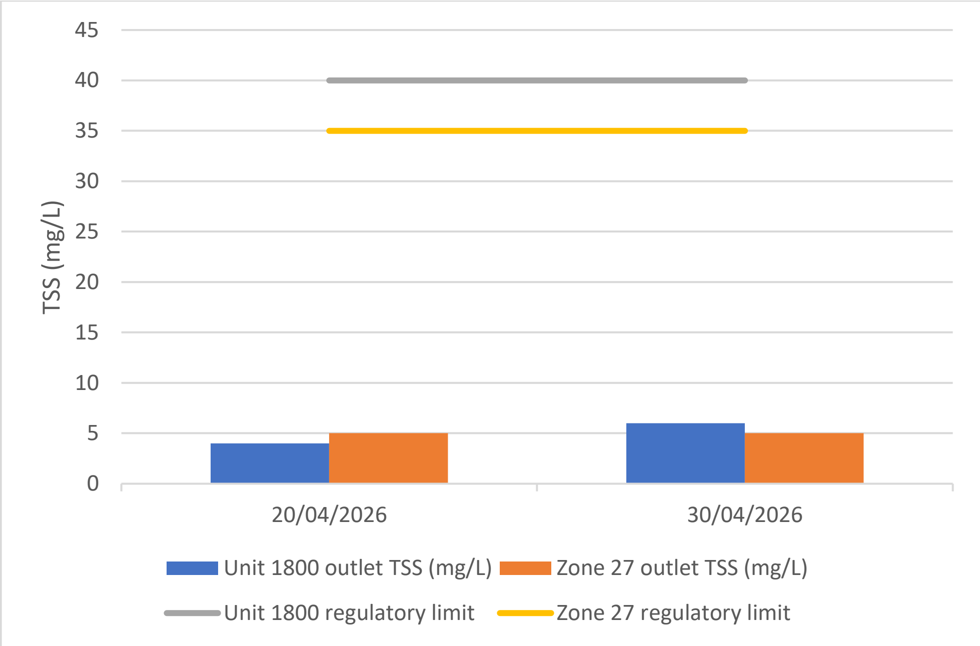


***Figure III.7:** Outlet TSS measurements compared with regulatory limits*

Figure III.7 shows that the outlet TSS concentrations of Unit 1800 and Zone 27 remained well below the regulatory limits during the selected measurements. This indicates good removal of suspended solids and suggests that clarification and filtration were effective for particulate matter reduction during the selected period. Therefore, TSS does not appear to represent a major compliance limitation in comparison with COD and BOD_5.

III.6.6 Outlet Conductivity

Conductivity is not the main regulatory parameter in this chapter, but it helps compare the mineral or ionic load between the two stations.

Figure (III.8) shows the variation of outlet conductivity versus time for Unit 1800 and Zone 27 during the selected period.

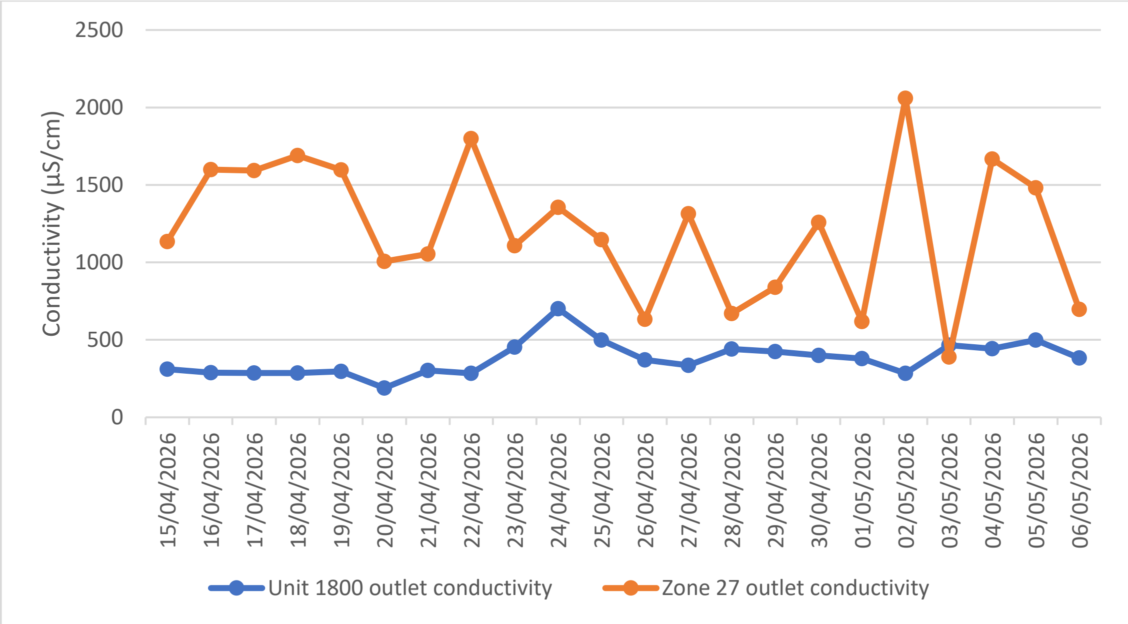


Figure III.8: *Outlet conductivity variation in Unit 1800 and Zone 27 during the selected period*

Figure III.8 shows that outlet conductivity was higher and more variable in Zone 27 than in Unit 1800 during the selected period. Unit 1800 presented relatively stable conductivity values, while Zone 27 showed several fluctuations and peaks, reaching values above 2000 µS/cm. This indicates that Zone 27 effluent contained a higher and more variable mineral load, which may be related to the nature of the influent and process drainage received by this treatment system.

III.6.7 Outlet of Furfural

Figure III.9 illustrates the temporal variation of the outlet furfural concentration for Unit 1800 and Zone 27 during the selected monitoring period.

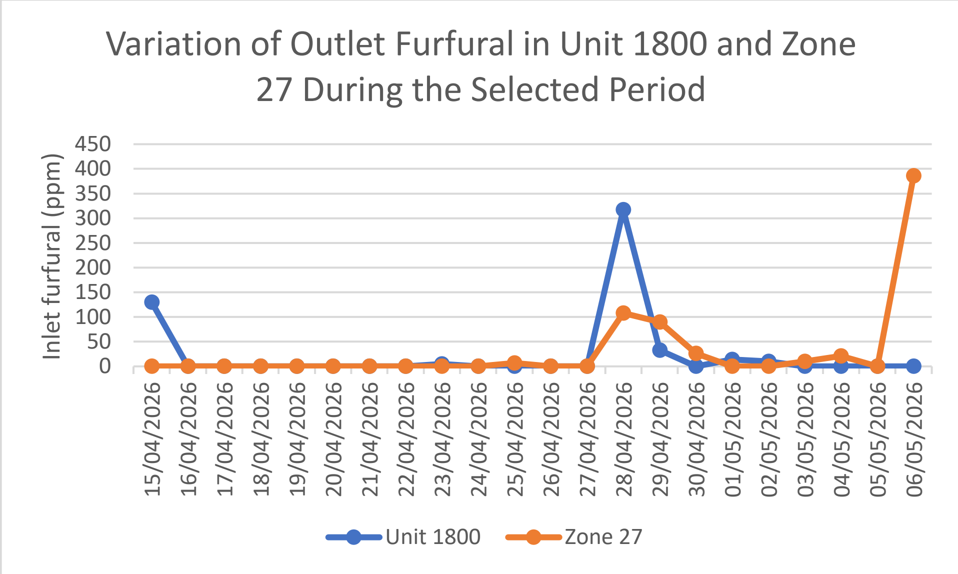


Figure III.9: Temporal variation of outlet furfural concentration in Unit 1800 and Zone 27 during the monitoring period

The outlet furfural concentrations in both Unit 1800 and Zone 27 remained close to zero for most of the monitoring period, indicating generally effective removal. However, a few significant peaks were observed, particularly in Unit 1800 on 28/04/2026 and in Zone 27 on 06/05/2026. These occasional increases may reflect temporary operational disturbances or unusually high influent loads. Since furfural is a toxic compound that should ideally be absent from the treated effluent, these peaks require careful monitoring and appropriate operational control to ensure consistent treatment performance.

Table III.3 summarizes the regulatory comparison of outlet quality for Unit 1800 and Zone 27 during the selected period.

Table III.3: *Regulatory comparison of outlet quality during the selected period*

Station	Parameter	Number of measureme	Minimum	Maximum	Average	Standard deviation
pH	Unit 1800	22	6.70-7.90	7.40	6.5-8.5	Compliant during the selected period

pH	Zone 27	22	6.30-8.30	7.35	6.5-8.5	One value below the lower reference; generally stable otherwise
Conductivity	Unit 1800	22	189-701	378.18	Not used as a direct limit here	Lower than Zone 27
Conductivity	Zone 27	22	390-2059	1214.00	Not used as a direct limit here	Higher mineral/ionic load
COD	Unit 1800	2	251-380 mg/L	315.50 mg/L	130 for old installation	Exceeds the reference in both measurements
COD	Zone 27	2	79-354 mg/L	216.50 mg/L	120 for new installation	One compliant value and one exceedance
BOD_5	Unit 1800	2	70-150 mg/L	110.00 mg/L	40 for old installation	Exceeds the reference in both measurements
BOD_5	Zone 27	2	20-140 mg/L	80.00 mg/L	35 for new installation	One compliant value and one exceedance
TSS	Unit 1800	2	4-6 mg/L	5.00 mg/L	40 for old installation	Compliant in both measurements
TSS	Zone 27	2	5-5 mg/L	5.00 mg/L	35 for new installation	Compliant in both measurements
HC	Unit 1800	22	0 mg/L	25 mg/L	7.77 for old installation	Generally compliant, with occasional peaks
HC	Zone 27	22	0 mg/L	39.3 mg/L	8.59 for new installation	*Generally compliant, with a few elevated values*

Furfural	Unit 1800	22	0 mg/L	317 mg/L	23.14 mg/L	High values
Furfural	Zone 27	22	0 mg/L	386 mg/L	29.82 mg/L	High values

The outlet quality evaluation shows that the treatment limitation is not the same for all parameters. pH and TSS were generally within the acceptable range, indicating stable pH conditions and good suspended solids removal. However, COD, BOD_5 and Furfural showed exceedances during some measurements, which indicates that residual organic pollution remained in the treated effluent. Therefore, the main outlet concern is related to organic load removal rather than suspended solids control.

III.7 Biodegradability and Biological Treatment Interpretation

The BOD5/COD ratio is used to interpret the biodegradability of the organic load. It is not a regulatory value. It helps assess whether the wastewater is easily biodegradable or whether it may contain refractory or toxic compounds.

Figure (III.10) shows the variation of the BOD_5/COD ratio versus time for Unit 1800 and Zone 27 during the selected period.

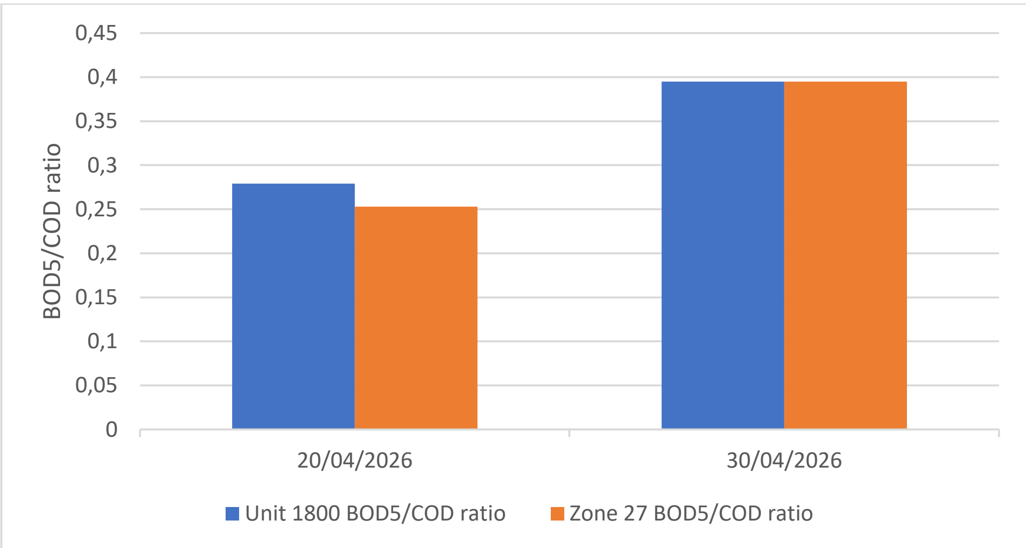


Figure III.10: *BOD5/COD ratio during the selected period*

Figure III.10 shows that the BOD_5/COD ratio varied between approximately 0.25 and 0.40 during the selected period. The values recorded on 20/04/2026 indicate limited to moderate biodegradability, especially for Zone 27. On 30/04/2026, the ratio increased for both Unit 1800 and Zone 27, indicating a higher biodegradable fraction of the organic matter. These results show that biological treatment can contribute to organic pollution removal, but its performance may be affected by the variability of influent composition and the presence of inhibitory compounds such as furfural.

Table III.4 presents the interpretation ranges used to evaluate the BOD_5/COD ratio and the biodegradability of the refinery effluent.

Table III.4: *Interpretation of the BOD5/COD ratio*

Station	Date	COD	BOD_5	BOD_5/COD ratio	Interpretation
Unit 1800	First available measurement	251	70	0.279	Low to moderate biodegradability
Unit 1800	Second available measurement	380	150	0.395	Moderate biodegradability, but high organic load
Zone 27	20 Apr. 2026	79	20	0.253	Low biodegradability, but COD and BOD5 remain controlled
Zone 27	30 Apr. 2026	354	140	0.395	Moderate biodegradability, but high organic load peak

The BOD_5/COD ratio indicates that the wastewater showed limited to moderate biodegradability during the selected period. This means that biological treatment remains useful, but its performance may be affected by variations in influent composition and by the presence of refractory or inhibitory soluble compounds. Therefore, the exceedances observed for COD and BOD_5 should be interpreted as a problem of unstable organic-load reduction, not only as a furfural-related problem.

III.8 Comparative Evaluation of Unit 1800 and Zone 27

Unit 1800 and Zone 27 cannot be compared as identical systems because their influent composition and design history are different. However, a comparative evaluation is useful because both stations treat refinery effluent and must ensure final effluent quality.

Table III.5: *Comparative interpretation of Unit 1800 and Zone 27*

Criterion	Unit 1800	Zone 27	Interpretation
Installation category	Old installation	New installation	Different regulatory references are required
Inlet hydrocarbons	Average 4.95%, maximum 17.00%	Average 6.11%, maximum 17.00%	Both stations receive variable oily loads
Inlet furfural	Average 89.37 ppm, maximum 588 ppm	Average 200.78 ppm, maximum 700 ppm	Zone 27 shows stronger furfural variability
Outlet pH	6.70-7.90	6.30-8.30	Generally stable pH
Outlet conductivity	Average 378.18	Average 1214.00	Zone 27 has higher mineral/ionic load
Outlet COD	251 and 380 mg/L	79 and 354 mg/L	Organic load peaks are observed
Outlet BOD_5	70 and 150 mg/L	20 and 140 mg/L	Unit 1800 exceeds in both available values; Zone 27 exceeds once
Outlet MES/TSS	4 and 6 mg/L	5 and 5 mg/L	Suspended solids removal is satisfactory in both stations
BOD_5/COD ratio	0.279 and 0.395	0.253 and 0.395	Biodegradability is variable and must be linked to organic load peaks

The comparison shows that suspended solids and pH are generally controlled, while the main concern is related to organic pollution and solvent-related variability. The presence of furfural peaks and high COD/BOD_5 values suggests that the biological stage may be exposed to harmful or unstable soluble loads.

III.9 Identification of the Main Treatment Limitation

The evaluation carried out in the previous sections shows that the main limitation is not related to the absence of treatment units. Both Unit 1800 and Zone 27 include several treatment stages, such as oil-water separation, physico-chemical treatment, biological treatment, and final polishing. However, the analytical results show that the outlet quality was not always stable during the selected monitoring period.

The comparison with regulatory reference values showed that pH and TSS were generally controlled in both treatment systems. This indicates that neutralization conditions and suspended solids removal were not the main limiting factors during the studied period. In contrast, COD and BOD_5 exceeded the regulatory reference values during some measurements, which confirms that residual organic pollution remained in the treated effluent.

At the inlet, the monitoring results also showed irregular variations in hydrocarbons and furfural, especially in Zone 27. These variations indicate that the treatment systems may receive variable oily and soluble organic loads. Such fluctuations can disturb downstream treatment stages, particularly biological treatment, when concentrated or inhibitory compounds reach the biological reactors.

Therefore, the main limitation retained in this chapter is the insufficient control of variable soluble and organic shock loads before biological treatment. This limitation can lead to unstable COD and BOD_5 removal at the outlet. Furfural is considered an important contributing factor because of its possible inhibitory effect on microbial activity, but it is not the only treatment problem. The outlet COD and BOD_5 exceedances show that the problem must be considered as a broader issue of organic-load stability and biological treatment protection.

For this reason, the proposed improvement should aim not only to reduce the impact of furfural-rich batches, but also to control high-COD, high-BOD_5, and combined soluble organic shock loads before they reach the biological treatment stage.

III.10 Selected Technical Solution

III.10.1 Principle of the Solution

The selected technical solution is based on the installation or use of a controlled dilution tank before biological treatment. The purpose of this tank is to receive wastewater batches characterized by high COD, high BOD_5, high furfural concentration, or combined soluble organic shock loads. Instead of allowing these concentrated batches to reach the biological reactors directly, they are temporarily collected, diluted with treated water, homogenized, and then gradually re-fed to the treatment line.

The objective of this solution is not to eliminate the pollutant mass by dilution. Its main purpose is to reduce the instantaneous concentration and shock effect of organic and inhibitory compounds reaching the microorganisms. By lowering sudden variations in pollutant concentration, the controlled dilution tank can help protect biological activity, improve process stability, and contribute to more regular COD and BOD_5 removal at the outlet.

III.10.2 Proposed Process Arrangement

Under normal conditions, the wastewater follows the existing treatment line:

$$Inlet\ effluent \rightarrow existing\ buffer/equalization \rightarrow API\ separation$$
$$\rightarrow physico-chemical\ treatment/flotation \rightarrow biological\ treatment$$
$$\rightarrow sand\ filtration \rightarrow discharge\ or\ reuse.$$

Under shock-load conditions, the proposed additional operating line is:

$$Furfural-rich\ or\ high-COD\ water\ phase \rightarrow diversion\ valve$$
$$\rightarrow controlled\ dilution\ tank \rightarrow mixing\ with\ recycled\ treated\ water$$
$$\rightarrow concentration\ check \rightarrow gradual\ feeding\ to\ biological\ treatment.$$

If furfural remains high after dilution, an optional activated carbon adsorption step can be used before gradual feeding.

III.10.3 Proposed Operating Rules

The proposed solution requires simple operating rules in order to decide when the controlled dilution tank should be used. Under normal operating conditions, the effluent can continue to follow the usual treatment line. However, when laboratory monitoring or operational observation indicates an abnormal organic or solvent-related load, the affected batch should be diverted to the controlled dilution tank.

The main operating rules proposed in this study are:

- If COD, BOD_5, furfural, or another relevant organic-load indicator exceeds an internal alarm threshold, the affected wastewater batch should be directed to the controlled dilution tank.
- The polluted batch should be mixed with recycled treated water in order to reduce the instantaneous concentration before biological treatment.
- The tank content should be homogenized before re-feeding to avoid sending concentrated zones directly to the biological reactors.
- The diluted wastewater should be gradually reintroduced into the treatment line at a controlled flow rate.
- The re-feeding step should be adjusted according to biological treatment stability, especially pH, dissolved oxygen, sludge condition, and outlet COD and BOD_5 evolution.

In this chapter, furfural is used as an important example of a solvent-related inhibitory compound, while COD and BOD_5 are used to evaluate the broader organic-load impact on outlet quality. Therefore, the proposed operating rules are not limited to furfural control only, but also aim to reduce the effect of high organic shock loads on biological treatment.

III.10.4 Expected Effect on Biological Treatment

The expected effect of the controlled dilution and gradual re-feeding solution is mainly related to the protection of the biological treatment stage. By reducing sudden variations in COD, BOD_5, furfural, and other soluble organic loads, the proposed tank can limit the direct exposure of microorganisms to concentrated or inhibitory wastewater batches.

This improvement can help maintain more stable biological activity, reduce the risk of microbial inhibition, and improve the regularity of organic matter removal. As a result, the outlet quality may become more stable, especially for COD and BOD_5, which were identified as the main parameters associated with organic pollution exceedances during the selected period.

Therefore, the proposed solution does not act as a complete treatment process by itself. It is a control and protection step designed to improve the operating conditions of the existing biological treatment system and reduce the impact of organic shock loads before final treatment.

Table III.6: Selected technical solution

Item	Selected solution
Main problem	Furfural-rich and soluble high-COD shock loads in the water phase may disturb biological treatment
Main target	Furfural, soluble COD? BOD_5, and solvent-related shock events
Sensitive stage	Biological treatment microorganisms
Selected modification	Controlled dilution tank using recycled treated water, followed by gradual re-feeding
Main equipment	Diversion valve, controlled dilution tank, mixing system, recycled treated water line, controlled feed pump, optional activated carbon unit
Operating mode	Normal flow continues in the existing line; shock-load batches are diverted, diluted, checked, and gradually fed to biological treatment
Expected effect	Reduced toxic shock, more stable biological treatment, and better COD/BOD_5 control

III.11 Preliminary Sizing of the Controlled Dilution Tank

The preliminary sizing of the controlled dilution tank is based on the need to reduce the instantaneous effect of soluble organic and solvent-related shock loads before biological treatment. In this section, furfural is used as a representative solvent-related shock parameter for dilution sizing, while COD and BOD_5 are used to evaluate the broader organic-load impact. Therefore, the proposed tank is not considered as a final treatment unit, but as a control, dilution, homogenization, and gradual re-feeding step intended to protect biological treatment and improve the stability of COD and BOD_5 removal.

III.11.1 Dilution Mass Balance

The controlled tank volume is estimated using a dilution mass balance. If a polluted batch is diluted with recycled treated water, the final concentration can be expressed as:

$$C_{final} = \frac{(C_b \times V_b + C_d \times V_d)}{V_b + V_d} \qquad \text{(III.3)}$$

If the recycled treated water contains negligible concentrations of the selected shock parameter, the equation becomes:

$$C_{final} = \frac{C_b \times V_b}{V_b + V_d} \qquad \text{(III.4)}$$

When the target concentration is fixed, the required total controlled volume is calculated as:

$$V_{total} = C_b \times V_b \,/\, C_{target} \qquad \text{(III.5)}$$

This equation gives the total controlled tank volume required to reduce the selected shock parameter from its peak concentration to the target concentration. The dilution water volume is then obtained from:

$$V_d = V_{total} - V_b \quad \text{(III.6)}$$

Furfural was selected as the representative parameter for the preliminary dilution sizing because it is a soluble solvent-related compound that may reach the biological treatment stage and affect microbial activity. Hydrocarbons were not used as the main sizing parameter because free and dispersed oil are mainly targeted by upstream oil-water separation and flotation units. Therefore, the controlled dilution tank is sized using furfural as a conservative shock indicator, while COD and BOD_5 are used later to evaluate the broader organic-load impact.

III.11.2 Preliminary Sizing for Unit 1800

For Unit 1800, the maximum observed furfural concentration during the selected period was approximately 588 ppm. The flow used for the preliminary estimate is 83 m^3/h. If the shock event is assumed to last one hour, the batch volume is:

$$V_b = 83\, m^3$$

Using a preliminary target concentration of 100 ppm:

$$V_{total} = (83 \times 588) / 100 = 488\, m^3$$

Therefore, the preliminary controlled dilution tank volume for one hour of furfural shock load in Unit 1800 is approximately:

500 m^3

The reduction of instantaneous concentration is:

Reduction = ((588 - 100) /588) x (100) = 83.0%

The corresponding dilution water volume is approximately 405 m^3.

$$V_d = 488 - 83 = 405\, m^3$$

This value represents the reduction of shock concentration, not real pollutant removal.

III.11.3 Preliminary Sizing for Zone 27

For Zone 27, the maximum observed furfural concentration during the selected period was approximately 700 ppm. The normal flow used for the preliminary estimate is 150 m^3/h. If the shock event is assumed to last one hour, the batch volume is:

$$V_b = 150\, m^3$$

Using a preliminary target concentration of 100 ppm:

$$V_{total} = (150 \times 700) / 100 = 1050\, m^3$$

Therefore, the preliminary controlled dilution tank volume for one hour of furfural shock load in Zone 27 is approximately:

1050 m^3

The reduction of instantaneous concentration is:

Reduction = ((700 - 100) / 700) x 100 = 85.7%

The corresponding dilution water volume is approximately 405 m^3.

$V_d = 1050 – 150 = 900\ m^3$

This value also represents shock concentration reduction rather than complete furfural removal.

III.11.4 Pollutant-Load Calculation for COD and BOD_5

Pollutant load calculations were performed for COD and BOD_5 using the available peak outlet values and the flow rates considered.

Table (III.7) presents the preliminary pollutant-load calculation for COD and BOD_5 used to evaluate the selected controlled dilution solution.

***Table III.7:** Preliminary pollutant-load calculation for the selected solution*

Station	Flow basis	Q (m^3/h)	Q (m^3/day)	Parameter	Average concentratio	Peak concentratio	Regulatory target used	Average load (kg/day)	Peak load (kg/day)	Target load (kg/day)	Required reduction at
Unit 1800	Maximum design flow	83	1992	COD	315.5	380	130	628.5	757.0	259.0	65.8
Unit 1800	Maximum design flow	83	1992	BOD_5	110	150	40	219.1	298.8	79.7	73.3
Zone 27	Normal flow	150	3600	COD	216.5	354	120	779.4	1274.4	432.0	66.1
Zone 27	Normal flow	150	3600	BOD_5	80	140	35	288.0	504.0	126.0	75.0

Zone 27	Design flow	200	4800	COD	216.5	354	120	1039.2	1699.2	576.0	66.1
Zone 27	Design flow	200	4800	BOD_5	80	140	35	384.0	672.0	168.0	75.0

The calculation shows that the strongest reduction requirement concerns BOD_5 during peak conditions. This supports the need to protect the biological stage from sudden organic and solvent-related loads.

III.11.5 Summary of Preliminary Controlled Tank Sizing

Table III.8: *Preliminary sizing of the controlled dilution tank*

Station	Flow used	Shock duration	Peak furfural	Target furfural	Estimated controlled tank volume	Reduction of instantaneous concentration
Unit 1800	83 m3/h	1 h	588 ppm	100 ppm	approximately 500 m3	83.0%
Zone 27	150 m3/h	1 h	700 ppm	100 ppm	approximately 1050 m3	85.7%

These volumes are preliminary engineering estimates. They must be validated using the real shock duration, existing available tank volumes, operational constraints, and the actual tolerance of the biological treatment system to furfural.

Although the preliminary sizing calculations were based on dilution principles, pollutant attenuation inside the proposed control system may also be interpreted using a transient mass-balance approach. For this reason, a simplified dynamic model is presented below to illustrate the effect of residence time and pollutant-removal kinetics on concentration evolution within the reactor.

III.11.6 Dynamic Mass Balance of Pollutant Removal

In this case, the accumulation term must be considered because, although the reaction mixture is assumed to be perfectly mixed and spatially uniform, its composition may vary with time. An open continuously stirred tank reactor (CSTR) is considered, operating under isothermal conditions with a constant flow rate and a constant reactor volume.

Figure (III.11) continuously stirred tank reactor (CSTR)

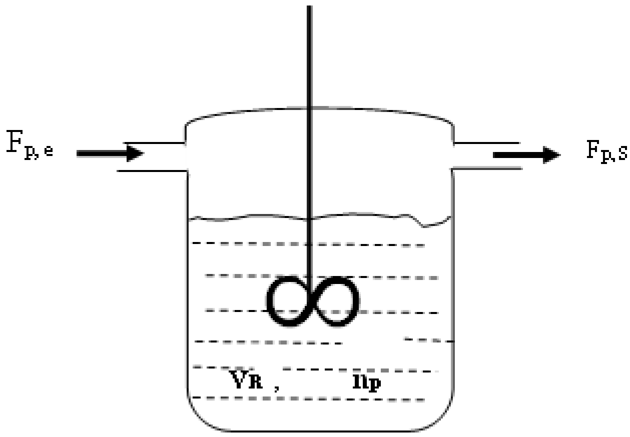


Figure III.11: continuously stirred tank reactor (CSTR)

III.11.6.1 Estimated Designs Data – Effluent Treatment Unit 1800

Parameter	**Value**
Treatment unit	Unit 1800
Reactor type	Rectangular reinforced concrete basin
Estimated length (L)	30 m
Estimated width (W)	15 m
Estimated water depth (H)	3 m
Estimated reactor volume (V)	1350 m^3
Maximum treatment flow rate (Q)	83 m^3/h
Hydraulic retention time (HRT)	16.27 h (976 min)
Mixing conditions	Complete mixing (CSTR assumption)
Kinetic model	Apparent first-order reaction
Operating temperature	Ambient (not specified in the manual)
Coagulant	Cationic polyelectrolyte

III.11.6.2 Estimated Design Data – Effluent Treatment Unit (Zone 27)

Parameter	**Value**
Treatment unit	Zone 27
Reactor type	Multi-compartment rectangular basin
Estimated geometry	Three interconnected rectangular compartments
Compartment 1	3 m × 2 m × 2 m
Compartment 2	10 m × 5 m × 3 m
Compartment 3	20 m × 10 m × 3 m
Estimated total volume (V)	762 m^3
Normal operating flow rate	150 m^3/h
Maximum design flow rate	200 m^3/h
Peak storm flow rate	3300 m^3/h
Hydraulic retention time (at 200 m^3/h)	3.81 h (229 min)
Mixing assumption	Complete mixing (CSTR assumption)
Kinetic model	Apparent first-order reaction
Coagulant	Cationic polyelectrolyte (pseudo-first-order assumption)

The general material balance for a pollutant may be written as:

$$F_{pe} + \nu_p r V_R = F_{ps} + \frac{dn_p}{dt} \quad \text{(III.7)}$$

where:

- F_{pe} : is the pollutant flux entering the reactor,
- F_{ps} :is the pollutant flux leaving the reactor,
- ν_p :is the stoichiometric coefficient,
- r :is the pollutant-removal reaction rate,
- V_R :is the reactor volume,
- $\frac{dn_p}{dt}$:is the pollutant accumulation term.

This is the general expression with the sole restriction that the reaction mixture is uniform throughout the reactor. We will apply this expression to the pollutant to be removed in the coagulation basin. According to the coagulation reaction occurring between the chemical coagulant (Coag) and the pollutant (P) present in the binary water–oil mixture, an insoluble complex is formed, as represented by the following overall reaction:

$$P_{sol} + Coag_{sol} \rightarrow PCoag_{\downarrow} \quad \text{(III.8)}$$

Assuming that the coagulant is present in excess, the reaction may be described using an apparent first-order kinetic model:

$$r_p = \nu_p\, r = -kC_{coag}C_p \quad \text{(III.9)}$$

Since the coagulant concentration is in excess, corresponding to the case of order degeneration (pseudo-order kinetics), we can write: $kC_{coag} = k_{app}$

and Equation III.9 can therefore be rewritten as follows:

$$r_p = -k_{app}C_p \quad \text{(III.10)}$$

$$C_{P0}Q - rV_R = C_{Ps}Q + \frac{d}{dt}(V_R C_{Ps}) \quad \text{(III.11)}$$

Where: C_{P0} is the concentration of pollutant P at the inlet, and C_{PS} is the concentration of P in the coagulation basin and at its outlet (perfectly mixed reactor).

Equation (III.8) then leads to the following expression:

$$\frac{dC_{Ap}}{dt} + aC_{Ap} = b \qquad \text{(III.12)}$$

This is a first-order differential equation with a constant nonhomogeneous term, where:

$$a = \frac{1+k\tau}{\tau} \text{ and } b = \frac{C_{A0}}{\tau}$$

Its analytical solution yields the following equation:

$$\frac{C_p}{C_{P0}} = \left[\left(\frac{k\tau}{1+k\tau}\right) exp\left(-\frac{C_{P0}}{\tau} \cdot t\right) + \frac{1}{1+k\tau}\right] \qquad \text{(III.13)}$$

This relationship shows that pollutant removal depends on both the apparent kinetic constant and the hydraulic residence time. Therefore, increasing residence time and reducing sudden pollutant peaks contribute to improved treatment efficiency and greater biological process stability.

When time is infinitely large ($t \to \infty$) equation (III.13) tends towards: $\frac{C_p}{C_{P0}} = \frac{1}{1+k\tau}$ (III.14) which is the steady-state equation.

Since no inlet concentration data were available, a hypothetical removal efficiency was assumed to estimate the apparent first-order reaction rate constant from the steady-state model.

From (Eq. III.14), the constant rate is obtained:

$$k = \frac{1}{\tau}\left(\frac{C_{P0}}{C_P} - 1\right) \qquad \text{(III.15)}$$

Furthermore, the removal efficiency, η , is defined as follows:

$$\eta = \frac{C_p}{C_{P0}} - 1 \qquad \text{(III.16)}$$

By combining (III.15) and (III.16), we obtain the relationship (III.17) which relates the apparent first-order rate constant (k), the hydraulic residence time (τ), and the pollutant removal efficiency (η):

$$k = \frac{1}{\tau}\left(\frac{\eta}{1-\eta}\right) \qquad \text{(III.17)}$$

The latter equation will be used to calculate the apparent first-order rate constants for a generic pollutant (P) in the coagulation basin.

1. For **Unit 1800**, the estimated hydraulic retention time is:

Assumed Removal Efficiency η	$\tau\ (h)$	**Estimated $k(h^{-1})$**
20%	16.27	0.246
80%	16.27	0.0154

2. For **ZONE 27**, the estimated hydraulic retention time is:

Assumed Removal Efficiency η	$\tau\ (h)$	**Estimated $k(h^{-1})$**
20%	3.81	1.05
80%	3.81	0.0656

The calculated values of the apparent first-order reaction rate constant k increase with increasing pollutant removal efficiency. This trend is consistent with the first-order kinetic model, in which higher removal efficiencies correspond to higher reaction rate constants. Furthermore, for the same assumed removal efficiency, the estimated k value is higher for Zone 27 than for Unit 1800 because of its shorter hydraulic residence time. These calculations illustrate the application of the proposed kinetic model under assumed operating conditions.

III.12 Conclusion

This chapter presented the engineering evaluation of the refinery wastewater treatment systems using analytical monitoring data, regulatory comparison, pollutant-load calculations, and biodegradability interpretation.

The results highlighted the occurrence of variable influent conditions and demonstrated that, despite generally satisfactory treatment performance, organic-load fluctuations may affect process stability and effluent quality. The analysis made it possible to identify the principal operational limitation and justify the need for an additional control measure upstream of biological treatment.

A controlled dilution and gradual re-feeding strategy was therefore proposed and supported through preliminary engineering calculations and mass-balance considerations. The obtained results provide a technical basis for improving the robustness of the treatment system under variable operating conditions and constitute the foundation for the overall conclusions of this work.

GENERAL CONCLUSION

General Conclusion

This work focused on the treatment of refinery oily wastewater and the evaluation of the existing treatment systems operating within the refinery. The study combined a review of refinery wastewater characteristics and treatment technologies with an assessment of actual operating data in order to identify the main factors affecting treatment performance and effluent quality.

The analysis was based on analytical data collected during the selected monitoring period and distinguished between influent characterization and treated-effluent quality assessment. Hydrocarbons and furfural were used as key indicators of variable and potentially harmful influent conditions, while pH, COD, BOD_5, TSS, and conductivity were used to evaluate treatment efficiency and compliance with regulatory reference values.

The results showed that pH and TSS were generally maintained within acceptable limits in both treatment systems. However, COD and BOD_5 occasionally exceeded the regulatory reference values (120 and 40 mg O_2 L^{-1}), indicating the persistence of residual organic pollution in the treated effluent. The BOD_5/COD ratio also revealed limited to moderate biodegradability, confirming that biological treatment remains effective but may be adversely affected by variations in influent composition and the presence of refractory or inhibitory soluble compounds.

The study identified insufficient control of variable soluble and organic shock loads upstream of the biological treatment units as the principal operational limitation. Although furfural was recognized as an important contributing factor because of its potential inhibitory effect on microbial activity, the observed treatment limitations reflect a broader issue related to fluctuations in organic loading and the protection of both chemical and biological treatment processes.

To address this limitation, a controlled dilution and gradual re-feeding strategy was proposed. The objective of this modification is to reduce the instantaneous concentration of high-COD, high-BOD_5, furfural-rich, and other concentrated soluble organic loads before they reach the biological reactors. The proposed solution is not intended to replace the existing treatment system but rather to improve its stability, enhance organic matter removal, and contribute to better effluent quality.

In addition to the experimental evaluation, a simplified engineering approach based on material balance and apparent first-order kinetics was developed to describe pollutant removal in the coagulation basin. This model made it possible to relate pollutant removal efficiency to hydraulic residence time and to estimate the apparent reaction rate constant under assumed operating conditions. Although based on simplifying assumptions, this approach provides a useful engineering framework for the preliminary evaluation and optimization of refinery wastewater treatment systems.

Overall, this work provided a better understanding of refinery oily wastewater treatment, evaluated the performance of the existing treatment facilities, and proposed a practical engineering solution to improve process robustness under variable operating conditions. Future work may focus on pilot-scale validation, detailed design optimization, and long-term monitoring of the proposed modification under industrial conditions.

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