Assessment of the Effectiveness of Available Pollution Control Technologies in Reducing Phenol Level at ENOC Refinery Wastewater Treatment Plant

Waddah Shihab Ghanim Al Hashemi
ASSESSMENT OF THE EFFECTIVENESS OF AVAILABLE POLLUTION CONTROL TECHNOLOGIES IN REDUCING PHENOL LEVEL AT ENOC REFINERY WASTEWATER TREATMENT PLANT

By

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B Eng (Hons.), Dip SM, Dip EM

Thesis submitted to United Arab Emirates University in partial fulfilment of the requirements for the Degree of M. Sc. in Environmental Science

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United Arab Emirates University
2005/2006
DEDICATION

IN THE NAME OF ALLAH, MOST GRACIOUS, MOST MERCIFUL

I dedicate this work to the Government of the United Arab Emirates and in particular to the Rulers of the Emirate of Dubai, which has seen great development and industrial diversification in the past 30 years due to the foresight and dedication of its Rulers.

I was and will remain particularly inspired by His late Highness Sheikh Zayed Bin Sultan Al Nahyan, President of the United Arab Emirates who was always committed to the practice of sustainable environmental development by “returning to the land the wealth it has given”, provided and supported this M.Sc. Program which I have been privileged to be part of.

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WADDAH SHIHAB M.A. GHANEM
APRIL, 2005
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<td>APHA</td>
<td>American Public Health Association</td>
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<td>API</td>
<td>American Petroleum Institute</td>
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<tr>
<td>BTEX</td>
<td>Benzene, Toluene, Ethyl benzene, and Xylene</td>
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<td>BOD&lt;sub&gt;5&lt;/sub&gt;</td>
<td>5-day Biochemical Oxygen Demand</td>
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<td>BPSD</td>
<td>Barrels Per Stream Day</td>
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<td>CLU</td>
<td>Central Laboratories Unit</td>
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<td>COD</td>
<td>Chemical Oxygen Demand</td>
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<td>DM</td>
<td>Dubai Municipality</td>
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<td>DO</td>
<td>Dissolved Oxygen</td>
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<td>EIA</td>
<td>Environmental Impact Assessment</td>
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<td>ENOC</td>
<td>Emirates National Oil Company</td>
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<td>EPA</td>
<td>Environment Protection Agency (US)</td>
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<td>EPCL</td>
<td>ENOC Processing Company LLC</td>
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<td>ETP</td>
<td>Effluent Treatment Plant</td>
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<td>FEA</td>
<td>Federal Environment Agency (UAE)</td>
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<td>GC-ECD</td>
<td>Gas Chromatography-Electron Capture Detector</td>
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<td>GC-MS</td>
<td>Gas Chromatography-Mass Spectrometer</td>
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<td>HDPE</td>
<td>High Density Polyethylene</td>
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<td>HSG</td>
<td>Health and Safety Guide</td>
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<td>I/L</td>
<td>Inlet</td>
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<td>Inorganic Carbon</td>
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<td>ICFBR</td>
<td>Immobilized Cell Fluidized Bed Reactor</td>
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<td>IGF</td>
<td>Induced Gas Flotation</td>
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<td>IPCS</td>
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<td>NTU</td>
<td>Nephelometric turbidity units</td>
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<tr>
<td>O&amp;G</td>
<td>Oil and Grease</td>
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<tr>
<td>O/L</td>
<td>Outlet</td>
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<tr>
<td>OWS</td>
<td>Oily Water Sewer</td>
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<tr>
<td>P&amp;ID</td>
<td>Process and Instrumentation Diagram</td>
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<tr>
<td>PAH</td>
<td>Poly-aromatic Hydrocarbons</td>
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<tr>
<td>PCB</td>
<td>Poly-chlorinated Biphenyls</td>
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<tr>
<td>PFBBr</td>
<td>Pentafluorobenzylbromide</td>
</tr>
<tr>
<td>pKa</td>
<td>Acid Dissociation Coefficient</td>
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P-450: A particular biological enzyme which catalyses the transfer of chemical groups between compounds (called P-450 transferase)
PLC  Process Logic Control
Pp  Pseudomonas Putida – A specific strain of bacteria
QA/QC  Quality Assurance/Quality Control
RAEEN  Risk Assessment and Environmental Exposure-Nitro-phenols
RBC  Rotating Biological Contactor
RNA  Ribonucleic Acid
SBR  Sequencing Batch Reactor
SWS  Sour Water Stripper
TC  Total Carbon
TCP  Trichlorophenol
TDS  Total Dissolved Solids
TOC  Total Organic Carbon
TOD  Total Oxygen Demand
TOG  Total Oil and Grease
TSS  Total Suspended Solids
UAE  United Arab Emirates
UOP  Universal Oil Products (USA based oil processing technology company)
US  United States
UV  Ultraviolet
VOPAK  a Dutch-based oil and chemicals terminating company/organization
WHO  World Health Organization
ABSTRACT

Phenols are present in discharge effluents of many heavy industries such as refineries. They are regulated and monitored by environmental authorities. Emirates National Oil Company (ENOC) processes condensate oil and produces wastewater that is treated at the ENOC Processing Company’s (EPCL-refinery) wastewater treatment plant (ETP) through the use of physical, chemical and biological treatment processes. This study provides an in-depth description of the unit processes employed to treat the different waste streams generated at the EPCL refinery and identifies the different types of phenols which are formulated in the processes. Characterization of phenol level at EPCL-ETP and assessment of the effectiveness of employed pollution control technologies in reducing phenol level at the treatment plant have been conducted in this study. In addition, the study explores the potential correlation between phenol level and other water quality parameters in the treated wastewater.

A thorough review of the adverse effects of phenols on the receiving environment has been provided in this study. It is well documented that phenol and its derivatives pose a danger to humans and marine life in their varying toxicities. Such toxicity depends on the solubility and persistence of the phenolic compounds in the system. The literature reveals that the sources and formation of phenol and its derivatives are based on many complex reactions.

It was found that the main sources of phenol in the received waste streams at ENOC-ETP are the crude oil tank wastewater drain (average 65.34 mg/l), the desalter effluent (average 0.95 mg/l) and the neutralized spent caustic (average 180 mg/l) waste streams. However, there are large fluctuations from the average phenol level within each waste stream. Also, the level of phenol and its derivatives in these streams vary significantly with phenol, m-p-cresols, o-cresol, tri and tetra-chlorophenols and to a lesser extent 4-chloro-3-cresol are common among these streams. Based on the average concentration from samples collected during this study and based on the average production of these streams, typical phenol loadings from tank wastewater drain, neutralized spent caustic and desalter wastewaters are 69.3 kg, 1497.8 kg and 131.5 kg per year, respectively. Other waste streams have been tested for phenol, but
the contribution of the other waste streams to phenol loading was found to be insignificant due either to the low flow rate or low phenol levels in the stream.

The processes employed in the treatment plant vary from a semi-continuous flow process (i.e. CPI, IGF) to a completely mixed batch reactor followed by continuous flow packed bed reactors. The study shows variations in water quality parameters at early stages of treatment but the waste stream is homogenized in the SBR and a more or less uniform treated waste stream enters the sand filter and the carbon bed.

The effluent in the wastewater treatment plant, basic odour, colour and clarity improves significantly through the stages of treatment. The study further showed that the most effective process employed in the reduction of phenols within the plant is the Sequencing Batch Reactors (SBR). This is also true for the organic loading which is reduced mainly by the SBR and to a lesser extent by the carbon reactor. The reduction of sulphides, like phenols, is almost entirely dependant on the performance of the SBR units.

Based on the analysis of five years (2000-2004) of daily data, it was found that the correlation between phenol level in the discharged treated effluent and levels of COD, BOD$_5$, and sulphides are weak although statistically significant in most cases. The relationship between BOD$_5$ and COD in the final effluent has been established with a ratio (COD:BOD$_5$) of 1.6 to 1 and an average non-degradable COD of about 55 mg/l. However, the relationship is again weak due to the scatter of the data as reflected by the low value of the coefficient of determination.

Recommendations are given mainly focusing on conducting further studies, such as characterization of waste streams at different condensate oil refineries, ETP performance, and process optimization. In addition, further investigation is needed to optimize SBR operations by characterizing and enriching microorganisms that specifically degrade phenol. It is also recommended to study the ETP performance on removal of other aromatic hydrocarbons.
CHAPTER ONE
INTRODUCTION AND OBJECTIVES

1.1 PREFACE

The development of the petroleum and petrochemical industry in the Arabian Gulf region has been rapid. In the last 50 years, exploration, drilling, extraction, refining and chemical engineering activities of oil and gas industry have all become essential components in the economy of many of the Arabian Gulf Countries. This speedy development has resulted in many changes such as landscape, economy, human development and interactions with other regions of the world as well as having impacts upon the environment and society. In fact “one of the most serious challenges facing the modern Middle East are the protection of its environment and the need to balance sustainable development with environmental security” [Morris, 2001].

Morris [2001] has summarized the main environmental problems in the region as:

1. Inadequate/ineffective legislation and control of pollution (into all water sources);
2. Increased industrialization with lack of proper effective environmental monitoring systems to detect and control this pollution and its subsequent impacts;
3. Improper location of industrial and urban development due to the pressures that town planning departments have faced due to the rapid growth after the surge of the financial resources from oil and gas into the economy.

While there are other environmental issues facing the region, the above three are considered the most salient.
The economic growth witnessed in the UAE in the last 3 decades coupled with lack of parallel adoption of environment management strategies has created many environmental challenges in the country. These challenges spread over a wide spectrum including air, water, and land pollution. To illustrate the magnitude of such challenges one has to look at national environmental figures like solid waste generation rate of 73 of 500-700 l/cap/d, pesticide application rate of 10 kg/ha/yr, etc [Gulf News, February 15th, 1999].

Water pollution is a serious concern in the UAE. This critical problem is made even more serious with the fact that water is very scarce in the region. Therefore, contamination of surface or groundwater resources has dire consequences. The Ministerial Order No. 37 Federal Environmental Law No. 24: 1999, Environmental Protection and Development, and under the Regulation for the Assessment of Environmental Effects of Installations/Developments (Annexure 1) requires an Environmental Impact Assessment (EIA) study before the execution of any refinery project [FEA, 1999]. Thus, the oil processing and refining projects are considered on the top of the list of projects requiring an EIA. In fact, such projects are also considered in a similar list in the UK-based Environmental Protection Act and the US-based Environmental Protection Agency set up under the National Environmental Protection Act (NEPA).

Oil refineries like most industries use enormous quantities of water. The used water contaminated with hazardous chemicals may be recycled/reused, treated, transported or released. Wastewater from oil refineries contains several pollutants (such as phenols, PCBs, PAHs, heavy metals and others) and requires appropriate treatment prior to discharge. Environmental regulatory agencies are beginning to enforce regulations seeking comprehensive solutions for facility licensing, permitting and enforcement issues. One of the pollutants of interest to this study is phenol.
Many studies have been conducted on the toxicity of phenols, and its derivatives, in various receiving environments. Phenol is a wastewater quality parameter that the regulators closely examine in the effluents/emissions from heavy industry such as refineries. Jebel Ali Free Zone Authority (JAFZA) in Dubai stipulates a maximum phenol level of 0.1 ppm for the discharge of wastewater from industries into the marine environment. Phenol removal from refineries can be achieved by either a single or combination of unit processes (physical, chemical, or biological).

No investigation has been made on the effectiveness of the commonly employed treatment processes for the removal of phenols from refinery wastewater in the UAE. Due to the severe adverse effects of phenol on the marine environment and the regulator requirements, it is essential to conduct such an investigation. Thus, the rationale behind this study stems from the fact that the Condensate Refinery ENOC Processing Company Ltd (EPCL) must comply with the regulatory requirements in the final effluent of treated wastewater. The treatment of effluent wastewater is, in fact, an integral part of the refinery operations that aims at reducing the adverse environmental impact of discharged effluents on the marine environment.

1.2 OBJECTIVES

The main objective of this study is to investigate the effectiveness of treatment processes employed at EPCL in reducing phenol levels in the wastewater generated by the refinery. Furthermore, the study identifies and characterizes troublesome streams that mainly contribute to phenol loading in the refinery wastewater. Specifically, the objectives of this study were:

1. Establish a baseline for phenol concentration of refinery wastewater typical to that generated at EPCL refinery.
2. Investigate possible existence of correlation between phenol and other wastewater parameters such as biochemical oxygen demand (BOD₃), chemical oxygen demand (COD), and sulphide in the effluent of the treatment plant.

3. Assess the effectiveness of the present operational units at the EPCL Effluent Treatment Plant (ETP) in reducing phenol.

4. Make recommendations on operational, engineering or maintenance changes to improve plant performance.

It is anticipated that this study will provide benchmark data for further studies that may be undertaken to assess the effectiveness and process optimization techniques that may be employed in improving the performance of treatment plants processing condensate refinery waste. Furthermore, salient points of this study may become the basic scope for further studies in the future.

1.3 APPROACH

The approach that is taken to achieve the above objectives includes characterization of potential streams making up the wastewater generated at the EPCL refinery for phenol level in order to identify the source of phenol. Samples from the inlet and outlet of each unit process of the treatment plant will be collected and analyzed for the target parameters such as temperature, pH, sulphides and total dissolved solids (TDS), BOD₃, COD, TOC, and phenol using standard test methods set by the American Public Health Association (APHA) and the US Environmental Protection Agency (US EPA). Individual phenols will be characterized in the effluents at each process by the EPA methods using both gas and high performance liquid chromatographic methods.
1.4 SCOPE OF WORK

The scope of this study will be limited to the analysis of samples taken during specific time periods and using previously collected data at EPCL. As such, the conclusions of this study are purely indicative of those periods and the basic behavior of the effluent treatment plant units. It should be noted that the types of effluents being processed at EPCL ETP are directly related to the crude condensate that is being processed upstream and stored in the refinery storage tanks.

Most samples are drawn at the same time and therefore the inlet conditions of one unit are assumed to be the same at the time the effluent entered the unit that processed the outlet sample. In the past batch effects such as slugs could have affected the individual results at the time of sampling and subsequent testing. Also, it is important to realize that the effluent in the final pond does not necessarily represent one batch. However, further testing over a 48 hour period using 6-hour samples was undertaken to establish fluctuation in parameter value of each unit process.

It is important to note that the refinery under study is a condensate refinery and not a full fledged heavy crude oil refinery, thus the effluent will have varying qualities as compared to that of crude oil refineries.

1.5 THESIS STRUCTURE

The thesis is presented in six chapters. Chapter 1 covers introduction, scope and objectives of this study. It also includes a brief discussion on the approach used to achieve the objectives and highlights the limitations of this work. Chapter 2 discusses the properties and some key reactions of phenols. It addresses the toxic properties of phenols and their effects on both humans and
marine life (based on an overview of the literature). It also discusses the sources of phenol from troublesome streams of the EPCL refinery based on discussions with EPCL operatives. Chapter 2 also includes a comparison between different regulations enforced in different countries/agencies in the world that regulate the disposal of treated wastewater. Chapter 3 an overview of the ENOC Processing Company Ltd (EPCL) (the first refinery in the emirate of Dubai) and the unit operations employed at its ETP. Chapter 4 addresses the sampling points/locations, sampling frequency as well as sampling and test methods employed in this study. Results obtained in this study are presented and discussed in Chapter 5. The chapter further presents historical data that were used to explore correlations between water quality parameters in the effluent of EPCL Wastewater Treatment Plant. Finally, Chapter 6 presents the conclusions (based upon the objectives outlined in Chapter 1), and outlines recommendations for further studies/development.
CHAPTER TWO

PHENOLS:
SOURCES, IMPACT AND DISPOSAL REGULATIONS

2.1 INTRODUCTION

The production/generation of industrial wastewater has steadily increased with the growth of various industries. Water being the most essential resource of life processes, must be carefully looked at especially in industrialized areas/countries. The discharge of industrial wastewater into water bodies will have different impacts based on its dilution and the living systems in the receiving environment.

Refinery wastewaters contain phenols along with other organic pollutants. Phenols are toxic to most living systems. Wastewater treatment plants, therefore, should reduce the phenol level in the wastewater and ensure that the levels are carefully controlled prior to its discharge.

This chapter is a literature review of the properties of phenol and its sources of existence in refinery wastewaters. The adverse effects and impacts of phenol on the living environment are reviewed with respect to discharges into the harbour and marine waters. In addition, the reduction of phenol through treatment is briefly discussed and evaluated in light of the experience of mainly the ENOC Processing Company Ltd (EPCL) that was established in Jebel Ali, Dubai, UAE in 1998.
2.2 PHENOL

2.2.1 Properties of Phenol

Phenol was discovered in 1834 when it was successfully isolated from coal tar. It was then named carbolic acid, which is in fact a name still used for liquid phenol containing more than 5% water by volume. The compound was not named phenol until 1841. Other synonyms of phenol include benzenol, oxy-benzene, phenic acid, phenyl hydroxide, cabolic acid, hydroxy-benzene, phenol, gescholzen and some others [Fremantle, 1991].

 Phenols include a wide variety of organic chemicals. These chemicals arise from the distillation of coal and wood and from oil refineries. Phenols may be classified into mono-hydridric, dihydric, and poly-hydric phenols depending on the number of hydroxyl groups attached to the aromatic ring. Phenol itself (Fig. 2.1), which has but one hydroxyl group, is the most typical of the group and the group is often used as a model compound. Phenol has an empirical formula of $C_6H_5OH$, a molecular weight of 94.11 g/mol, and is composed of 76.57% carbon, 17.0% oxygen and 6.43% hydrogen. At 25°C it is a clear, colourless, hydroscopic, deliquescent, crystalline solid, and changes colour if impurities exist [Rave and Hageman, 1989].

![Fig. 2.1: Structure of Phenol](image-url)

When stored in shore tanks, there is usually some kind of heating facilities for the tank with mixers to keep the phenol liquid in colder climates. Also, there is usually heat tracing on the transfer lines on all terminals handling phenol. It melts at about 40 to 43°C and boils at about 181.75°C [Nuffield, 1984]. It has a vapour pressure of about 0.35 mm Hg at 25°C. In its solid form, phenol has a specific
gravity of about 1.071 and 1.049 in the liquid form. Phenol has a high solubility in water of 62 g/l at 16°C, with the amount dissolved increasing with increase in temperature. Phenol is also soluble in organic solvents such as benzene, alcohol, chloroform, ether, glycerol, carbon sulphide, and petrolactum. The octanol-water partition coefficient for phenol is 31 [Rave and Hageman, 1989].

Phenol when produced is generally recovered from coal tar, and considerable amounts are manufactured synthetically. It is used extensively in the synthesis of organic compounds and in particular phenolic-type resins. It occurs as a natural component in industrial wastes from the coal-gas, coal-coking, and petroleum industries as well as in a wide range and variety of industrial wastes from processes involving the use of phenol as a raw material.

Phenol has a characteristic smell and like alcohols, phenols have higher boiling points than one might expect. This is due to the intermolecular forces of hydrogen bonding. For example to draw a comparison, 2-nitro-phenol has a lower boiling point than 4-nitrophenol which is due to the fact that the former molecule exhibits intra-molecular forces whereas the latter molecule has more intermolecular bonding forces and is thus less volatile. Phenol is both moisture and light sensitive and reacts violently with oxidizing agents. It is a stable compound but can burn explosively when heated. Phenol is only partially miscible with water at temperatures less than 66°C [Hart et al., 1991].

Phenol can be prepared in the laboratory by fusing the anhydrous sodium salt of benzenesulphonic acid with solid sodium hydroxide between 300 and 350°C and then followed by the addition of hydrochloric acid in the reaction as shown below [Fremantle, 1991].
2.2.2 Common Properties and Reactions of Phenols

Phenol exhibits weakly acidic properties with a pKa value of about 9.95. Thus, it is slightly acidic although it is still a stronger acid than methanol, ethanol and water. The phenolate ion produced by the loss of an H\(^+\) ion is stabilized by de-localization of the negative charge [Nuffield, 1984].

Like alcohols, phenols react with strongly electropositive metals such as sodium to produce hydrogen. However, unlike alcohols, phenols react with sodium hydroxide. It is not as strong an acid as the carboxylic acids, such as ethanoic acid or benzoic acid which liberate carbon dioxide from sodium hydrogen-carbonate or sodium whereas phenol does not. This reaction is in fact used to distinguish between carboxylic acids and phenols.

Although phenol does not react with carboxylic acids to form esters, it does react with acid chlorides in alkaline solutions in reactions called acylation reactions. Phenols also react with halogeno-alkanes under alkaline conditions to form ethers and these reactions are an example of what is known as Williamson’s Synthesis. The reaction of phenol with phosphorus penta-chloride works and unlike

![Fig. 2.2: Laboratory preparation of phenol.](image)
alcohols, phenol does not react with hydrogen halides or phosphorous trihalides. However, it does react slowly with phosphorus penta-chloride to poorly yield a chloro-benzene [Fremantle, 1991].

Iron (III) chloride, when in a neutral solution and then added to phenol, a complex is formed with a distinct violet colour. This is generally used as a test for phenol. This reaction is also generally characteristic of compounds containing the -enol group. It is very critical to understand how the benzene ring behaves in phenol because phenol undergoes electrophilic substitution more readily than benzene alone. This is basically because the non-bonding electrons on the oxygen atom are drawn into the ring, and thereby activate the ring. The hydroxyl group is a 2,4-directing with respect to the electrophilic substitutions.

Halogenation reactions with phenol occur under much milder conditions when compared to similar reactions with benzene alone. For example, when bromine water is added to an aqueous solution of phenol, a white precipitate of 2,4,6-tribromophenol is formed. Besides UV, the reaction requires a Lewis catalyst (typically iron (III) bromide and aluminium chloride). These compounds work by the induction of polarization in the halogen molecule, which forms a complex with the catalyst. Thus, an interim bromide complex must be formed and then the bromo-benzene is formed in addition to hydrogen bromide and iron (III) bromide in the regeneration of the catalyst [Fremantle, 1991; Hart et al., 1991].

Phenol can also undergo nitrification using diluted nitric acid. In this reaction about 70% of the yield is 2-nitrophenol and 30% is 4-nitrophenol. When compared to benzene these are very mild conditions. As such benzene requires a concentrated mixture of both nitric and sulphuric acid for nitrification to occur [Hart et al., 1991]. The 2-nitrophenol and 4-nitrophenol are much stronger acids than phenol and this is due to the nitro group being a strong electron withdrawer. As a result, the benzene ring withdraws more electrons from the oxygen atom in the hydroxyl group.
In the sulphonation reactions, concentrated sulphuric acid reacts with phenol to produce a mixture of hydrobenzenesulphonic acid in a proportion of 15 and 85% yields for 2-hydrobenzenesulphonic acid and 4-hydrobenzenesulphonic acid, respectively. This is only true for concentrated acid addition in the reaction. The two products are formed in this reaction with concentrated nitric acid to form a 2,4,6-trinitrophenol. This is a yellow crystalline solid called picric acid. Due to the combination of the withdrawing power of the three nitro groups, picric acid is a relatively strong organic acid. It has a pKa value of 1 and will liberate carbon dioxide from sodium carbonate solution [Fremantle, 1991; Hart et al., 1991].

With reference to coupling reactions, an alkaline solution of phenol reacts with benzenediazonium chloride solution to form an orange precipitate of 4-hydroxyphenylazobenzene. This product is called an azo dye and this reaction is an example of a phenol coupling reaction. Phenols volatility is quite high and ranks one of the highest in terms of typical organic contaminants in wastewaters. The Henry's constant ($K_H$) is approximately $4.57 \times 10^7$ atm-m$^3$/mol at 20°C. In general, if the $K_H$ constant value exceeds 0.01 atm-m$^3$/mol, the compound can be removed easily by air stripping. Moreover, when compared to other compounds the water solubility is very high (93000 mg/l at 20°C) whereas that of benzene is about 1780 mg/l, for toluene is 100 mg/l, and for 2-nitrophenol is 2100 mg/l. This may explain the high mobility of phenol in aqueous systems [Sawyer et al., 1994].
2.2.3 Phenol Derivatives

There are various types of phenol derivates and compounds which may exist in petroleum hydrocarbons and thus in refinery wastewaters. This section will discuss in brief the different types of phenols that may exist in the wastewater and treated waters. These phenols are primarily cresols, chlorophenols and nitro-phenols.

2.2.3.1 Cresols: [WHO, IPCS, HSG 100, 1996]

*Physical and Chemical Properties:* Cresols are isomeric substituted phenols with a methyl substituent at one of the $o$-, $m$-, or $p$- positions relative to the OH-group (Fig. 2.3) with a molecular formula $C_8H_{10}O$ and a molecular mass of 108.14. Physically, they are white crystalline solids or yellowish liquids with a strong phenol-like odour. The compounds are highly flammable, moderately soluble in water and soluble in ethanol, ether, acetone, or alkali hydroxides chemically, these alkyl phenols undergo electrophilic substitution reactions at the vacant $o$- or $p$-positions or undergo condensation reactions with aldehydes, ketones, or dienes. The melting points range between 12.22 to 34.74°C for $m$, $o$ and $p$-cresols respectively. The flash-point of cresols is between 80 and 85°C and the ignition temperature for all three isomers is 558°C. Other information on the full chemical and physical quality can be referred to from standard books of reference data.

![Diagram of cresols](image)

Fig. 2.3: Examples of cresols
**Analysis of cresols:** Cresols can be detected and quantified in a number of environmental and biological samples. The most common methods for determining the presence of cresols are gas chromatography (GC) and high-performance liquid chromatography (HPLC). Sample detection limits are typically around 4-10 μg/l in water for all cresols.

**Production and Uses:** Although cresols and cresol derivatives occur naturally in the oils of various flowering plants and trees, such as jasmine, Easter lily, yucca, conifers, oaks, and sandalwoods and even p-cresol is found in the urine of animals and humans. Commercially, cresols are produced as by-products in the fractional distillation/refining of crude oil and coal tars and in coal gasification. The various isomers can be manufactured and formed by the methylation of phenols, toluene sulfonation and alkaline hydrolysis, or the hydrolysis of 2-isopropyltoluene or alkaline chlorotoluene. Cresols have a wide variety of uses as solvents, disinfectants, or intermediates in the preparation of numerous products. They are commonly used in the production of fragrances, antioxidants, dyes, pesticides, and resins. In addition, p-cresol is used in the production of lubricating oils, motor fuels, and rubber polymers while m-cresol is also used in the manufacture of explosives.

**General Human/Marine Life Exposure Hazards:** The general population can be exposed to cresols through air inhalation, drinking-water, food, and beverage ingestion, and dermal contact. In general, the lack of adequate monitoring data make the quantitative estimate of daily intakes of cresol from these sources impossible. Occupational exposure levels in air as high as 5.0 mg/m³ have been reported. Cresols, at concentrations normally found in the environment do not pose any significant risk for the general population. However, the potential for adverse health effects exists for specific sub-populations and under conditions of high exposure. No information is available regarding the effects of long-term exposure to cresols. Thus, information to assess the carcinogenic hazard of cresols is inadequate. As far as the impacts on marine life, observations on microorganisms, invertebrates, and fish show that cresols may present a risk for non-mammalian organisms at point sources with high cresol concentrations, but not in the general environment.
Physical and Chemical Properties: Chlorophenols can form in processing of hydrocarbon and wastewater. Chlorophenols vary in molecular weights depending mainly on the number of chlorine substituents on the ring (Fig. 2.4). The molecular formulas are \( \text{Cl}_n\text{C}_6\text{H}_4\text{OH} \), \( \text{Cl}_2\text{C}_6\text{H}_3\text{OH} \), \( \text{Cl}_3\text{C}_6\text{H}_2\text{OH} \), \( \text{Cl}_4\text{C}_6\text{H}_2\text{OH} \) and \( \text{Cl}_5\text{C}_6\text{H}_2\text{OH} \) for the single, double, triple, tetra and penta-chlorophenols, respectively. Thus the molecular weights range from 128.5-266.5 for the previous compounds. The boiling points, melting points and densities increase with the number of chlorine substitutions. Although the vapour pressure remains the same, the water solubility is drastically reduced with increase in substitutions. The water solubility (in mg/l) is reduced from 28,000 to 900 from the single to the trichlorophenol [WHO, 1996].

Analysis of chlorophenols: EPA methods 604 [US EPA, 1985], 525 [US EPA, 1988] and 8270 [EPA, 1986] are used for the determination of chlorophenols. The most sensitive technique involves the formation of the pentafluorobenzyl ether derivatives (an option in method 604); the method has a detection limit of 0.5–5 µg/l. Chlorophenols can also be determined by gas chromatography with an electron-capture detector. The detection limits are 1–10 µg/l for monochlorophenols, 0.5 µg/l for dichlorophenols, and 0.01 µg/l for trichlorophenols [Traud, 1978].
EPA methods 604 [US EPA, 1985], 525 [US EPA, 1988] and 8270 [EPA, 1986] are used for the determination of chlorophenols. The most sensitive technique involves the formation of the pentafluorobenzyl ether derivatives (an option in method 604); the method has a detection limit of 0.5–5 μg/l. Chlorophenols can also be determined by gas chromatography with an electron-capture detector. The detection limits are 1–10 μg/l for monochlorophenols, 0.5 μg/l for dichlorophenols, and 0.01 μg/l for trichlorophenols [Traud, 1978].

![Chemical structures of chlorophenols](image)

**Production and Uses:** Chlorophenol (2-CP) is used as a precursor in the production of higher chlorophenols and dyestuffs, and as a preservative. 2,4, dichlorophenol (2,4-DCP) is used as a mothproofing agent, germicide and antiseptic, and in the production of the pesticide 2, 4 dichlorophenol (2,4-D). The 2,4,6 trichlorophenol (2,4,6-TCP) is used in the production of 2,3,4,6-tetrachlorophenol and pentachlorophenol, and as a germicide, glue, wood preservative, and antimalarial agent [Feiter, 1979; Doedens, 1936].

**General Human/Marine Life Exposure Hazards:** Chlorophenols are present in drinking-water as a result of the chlorination of phenols during disinfection, as by-products of the reaction of
hypochlorite with phenolic acids, as biocides, or as degradation products of phenoxy herbicides. Data from 40 Canadian treatment plants indicate that chlorophenol levels in drinking water are generally quite low but vary considerably from one location to another [Sithole and Williams, 1986]. Chlorination increased the concentrations of 2-CP (maximum 65 ng/l), 2,4-DCP (72 ng/l), and 2,4,6-TCP (719 ng/l). Drinking-water from the Ruhr area of Germany contained 2,4-DCP at 36 ng/l and 2,4,6-TCP at 1 ng/l [Traud, 1978].

Chlorophenols are well absorbed after oral administration [Carpenter et al., 1985], and they readily penetrate the skin [Roberts et al., 1977]. Chlorophenols do not appear to accumulate in body tissues in rats but are rapidly metabolized and eliminated from the body [Somani et al., 1982]. The major metabolite is the glucuronide conjugate of the parent chlorophenol. Less abundant metabolites include sulfate conjugates and possibly chloro-methoxyphenol isomers of the parent compounds [Carpenter et al., 1985]. Chlorophenols are readily excreted as glucuronide conjugates in urine and, to a lesser extent, faeces [Korte et al., 1978].

2.2.3.3 Nitro-phenols [WHO, IPCS, HSG 20, 2000]

Physical and Chemical Properties: The nitro-phenols (o- and p-nitro-phenol) share the imperial formula of C₆H₅NO₂ and both have a molecular mass of 139.1 (Fig. 2.5). The melting points range between 44-45°C for 2-nitrophenol and 113-114°C for 4-nitophenol. The boiling points also differ with 216 and 279°C for the 2-nitro and 4-nitro isomers, respectively. The water solubility of 4-nitrophenol is significantly higher at about 12.4 g/l as opposed to 1.26 g/l for 2-nitro-phenol. They both have a similar dissociation constant at 21.5°C [WHO, 2000].
The analytical methods for the determination of nitro-phenols are usually GC detection but they also can be detected using the flame ionization methods and electron capture methods. Generally, a solid-phase adsorption method with thermal or extraction from water samples is undertaken.

Production and Uses: Nitro-phenols are not found naturally and are therefore chemically synthesized by specialist manufacturers. Both are used as intermediates in the synthesis of azo dyes and a number of pesticides, mainly insecticides and to lesser extent herbicides. [WHO, 2000]

General Human/Marine Life Exposure Hazards: Nitro-phenols have some impacts on human beings. The following is an extract from the executive summary of WHO International Program on Chemical Safety publication: “There is only limited information concerning the toxicological profiles of 2- and 4-nitrophenol. In experimental animals given 4-nitrophenol orally, intravenously, or otherwise most of the applied dose was excreted via the urine within 24-48 hr as glucuronid and sulfate conjugates, while only very small amounts were excreted via faeces or as unchanged 4-nitrophenol. The percentages of glucuronide and sulfate conjugates were shown to be species and dose dependent. After oral dosing in rabbits, 4-nitrophenol undergoes reduction to p-aminophenol as well as glucuronidation and sulfation [WHO, 1996].
The available data from *in vivo* and *in vitro* studies give an indication for dermal uptake of 4-nitrophenol. The data for 2-nitrophenol are very limited, however, based on the available data a comparable metabolic transformation is assumed. Bioaccumulation of 2- and 4-nitrophenol in organisms is not to be expected owing to its rapid metabolism and excretion. In acute studies, 4-nitrophenol is harmful after oral uptake and was found to be more toxic than 2-nitrophenol. A dose-dependent increase in the formation of methaemoglobin was seen in cats after oral exposure to 2-nitrophenol and in rats after exposure by inhalation to 4-nitrophenol. After repeated exposure to 4-nitrophenol, the formation of methaemoglobin was shown to be the most critical end-point for exposure by inhalation and is assumed to be relevant for oral exposure too. Other noted effects included decreases in body weight gain, differences in organ weights, focal fatty degeneration of the liver, and haematological changes. For these effects, it was not possible to identify a clear dose-response. 2-Nitrophenol is slightly irritating to the skin but non-irritating to the eye. The substance proved to have no sensitizing effects in a Buehler test. Based on valid studies with experimental animals, irritating effects on skin and eye are assumed for 4-nitrophenol. In a guinea-pig maximization test, 4-nitrophenol was considered as slightly sensitizing. In humans, a possible sensitization after contact with 4-nitrophenol cannot be excluded, especially as skin sensitization has been found in patch tests on factory workers who may have been exposed to 4-nitrophenol. Neither of the two isomers of nitro-phenol has been fully tested for geno-toxicity. Insufficient data are available on 2-nitrophenol to allow any conclusions to be made about its possible mutagenicity. More mutagenicity studies are available for 4-nitrophenol, although some were inadequately reported.

There are some registered effects on marine life with relative toxicities that may affect the marine life to different magnitudes. This issue was briefly researched and an extract is provided from the WHO International Program on Chemical Safety Publication.
“Among all tested organisms, the protozoan Entosiphon sulcatum and the green alga Scenedesmus subspicatus proved to be most sensitive in chronic cell multiplication inhibition tests with freshwater species. Daphnia magna exhibited a 21-day lowest-observed-effect concentration (LOEC) of 1.0 mg 2-nitrophenol/litre in the Daphnia reproduction test [Koerdel et al., 1984]. The entoproct Barentsia matsushimana was the most sensitive marine invertebrate species tested, exhibiting a 49-day EC50 value of 0.21 mg 4-nitrophenol/l and a minimal effective concentration (ECm) of 0.03 mg/l (end-point: growth of germinated spores) [Scholz, 1986]. Freshwater fish showed less sensitivity. The lowest 96-h LC50 value of 3.8 mg 4-nitrophenol/l was determined for rainbow trout (Oncorhynchus mykiss) [Howe et al., 1994]. The measured no-observed-effect concentration (NOEC) for behavioural changes in a 28-day flow-through test with zebra fish was 2 mg 2-nitrophenol/l [Broecker et al., 1984]. After prolonged exposure of zebra fish to 4-nitrophenol, minor morphological alterations of the liver, even at a concentration of 0.1 mg/l, were observed. At 1 and 5 mg/l, about 25% of the animals showed symptoms of degenerative transformation of the liver tissue [Braunbeck et al., 1989].”

2.3 ENVIRONMENTAL IMPACT OF PHENOL

2.3.1 Toxicity of Phenol

The effect of phenol toxicology is through interference with the different types of bio-transformations in conjugation reactions such as oxidation, reduction, glycuronide and glycine. As an example in the phenolic hydroxyl and some more aromatic nitro compounds become amines with the hydroxy-amines and aliphatic carboxylics do not, except in the instances where the latter group is attached to a tertiary carbon atom. Both stable ether-type and unstable ester-type glycuronides are formed, depending on the group conjugated.

After absorption in the body, chemicals can be converted to less toxic, non-toxic, or more toxic derivatives by the P-450 monooxygenases located in the liver microsomol smooth endoplasmic reticulum. Arene oxides are intermediates in the bio-transformation of phenols,
trans-dihydriols, and permercapturic acids, and their steady-state concentrations are related to rates of formation and the ability to isomerize to phenols, react with the glutathion, and undergo enzymatic hydration. Cytotoxicity is caused by these intermediates, which covalently bind to tissue macromolecules. Epoxide hydrases are involved in the transformation of arene oxides to potent epoxides. Gluthione conjugation of arene oxides is a major pathway that significantly affects their tissue concentration and any process that depletes liver glutthion concentrations can produce serious toxic effects [Haley et al., 1987].

2.3.2 Human Exposure to Phenols

Phenol has some critical hazards to humans. The substance is caustic and hazardous. It can enter the organism via the skin, by inhalation or by ingestion. It is corrosive to eyes, skin and the respiratory system. According to the National Fire Protection Association (based on substance UN number), phenol is ranked at number 4 (on a scale of 0 to 4) from a health hazard point-of-view [VOPAK Organisation, 2002].

The ingestion of small quantities of phenol can cause or induce vomiting, circulatory collapse, tachypnea, peralysys, convulsions, coma, greenish or smoke coloured urine, necroses of the mouth and gastrointestinal tract, icterus, death by suffocation and at times cardiac arrest. The US EPA classified phenol as one of the priority pollutants [US EPA, 1979]. With respect to chronic toxicity it is similar to acute toxicity but by lesser amounts of phenols over extended periods [Haley et al., 1987]. The LD50 for phenol (oral-rat) is 317 mg/kg and for dermal-rat contact it is 669 mg/kg [VOPAK Organisation, 2002]. Some studies have shown that phenol in a concentration of 1 μg/l would not interfere with domestic water supplies [Mckee and Wolfe, 1963].
Phenol has deleterious effects on the water quality especially in the presence of chlorine. This is clearly reflected by setting the maximum allowable concentration of phenol in drinking water to 0.001 mg/l for chlorinated water as compared to 1.0 mg/l for non-chlorinated water. Problems with chlorinated phenols in drinking water supplies stem from the fact that phenol is not removed efficiently by the traditional and conventional methods of water treatment. [Albersmeyer and von Erichsen, 1959]. Reaction of phenol with chlorine results in the formation of more odorific compounds and perhaps more toxic as well. The EPA has observed, however, that there is no demonstrative relationship between organoleptic and human health effects, for drinking water at or below the standards [US EPA, 1979].

2.3.3 Impacts of Phenol on Marine Aquatic Life

Phenols are categorized as highly persistent and toxic pollutant in marine environment. They enter coastal waters through wastewater discharges from a wide range of chemical and petrochemical industries that include refineries and oil/gas processing. Presence of phenol in a lake or a river has serious effects on aquatic life, and the taste and odour of fish. For example; taste and odour of edible fish on average is affected at 15-25 mg/l phenol concentration.

The impact of phenolic compounds on water quality is even tangible at trace levels (<1 mg/l). The recent EPA criterion for phenol is set at 3.5 mg/l to prevent most toxic effects to saltwater and freshwater aquatic species [US EPA, 1979]. The 1975 criterion was set at 1 μg/l for both surface and domestic water supplies where chlorination is used. For comparison, EPA estimated that a level of 0.3 mg/l would be necessary to control undesirable taste and odour of ambient water [US EPA, 1979]. It is important to note that most studies analyse for concentration of phenolic compounds rather than phenol alone, especially when studying the effects on marine life [Rave and Hageman, 1989].
Generally the lethal-dose 50 (LD50) phenol is 5 mg/l for fish. However, phenolic compounds impart a broad spectrum toxicity depending upon type and position of substitution in the actual ring in the molecule. For example, LD50: trout embryos are 2 mg/l for o-cresol [VOPAK Organisation, 2002].

Studies have shown that some environmental conditions will increase the toxicity of phenol. Based on studies conducted by the European Inland Fisheries Advisory commission [1973], lower dissolved oxygen concentrations, increased salinity, and increased temperature all enhance the toxicity of phenol. It has also been shown that phenol and o-cresol have a 24 hour LC-50 of about 5 and 2 mg/l, respectively, for trout embryos [Albersmeyer and von Erichsen, 1959]. Rainbow trout were killed in 7.3 mg/l phenol in 2 hours and in 6.5 mg/l phenol in 12 hours. At these concentrations there was rapid damage to gills and severe pathological effects on other tissues [Mitrovic et al, 1968]. Also pathological changes in gills and in fish tissues were found at concentrations in the range of 20 to 70 µg/l [Reichenbach et al., 1965].

In some review of the literature it was found that low concentrations of about 200 µg/l may interfere with aquatic life. Most of the heterotrophic material and yeast isolates from mangrove swamps could tolerate and grow at 0.5% concentration of phenol [Mckee et al, 1963]. Shumway [1966] estimated threshold fish flesh tainting concentrations from 0.1 to 15 µg /l. The o-chlorophenol produced tainting at even lower concentrations [Shumway, 1966].

Phenolic compounds can affect freshwater fish adversely by direct toxicity to fish and fish-food organisms; by lowering the amount of available oxygen because of the high oxygen demand of the compounds and perhaps by tainting the fish tissue and flesh. Studies conducted
such as those by the European Inland Fisheries Advisory Commission [1973] confirmed the adverse effects of phenol on adult and immature organisms. Moreover, an investigation on oysters showed that phenol results in a decrease in egg development at levels of about 2 mg/l [Davis and Hidu, 1969].

A major aesthetic problem associated with phenolic compounds is their organoleptic properties in water and fish flesh. Threshold odour levels range from 55 μg/l of p-cresol to about 2 μg/l for 2-chlorophenol based on studies conducted by various researchers [Rosen et al., 1962; Burttchell, 1959].

2.3.4 Effects of Phenol on Micro-organisms

Presence of phenol in many cultures, even at low concentrations, has deleterious effect on the activity of micro-organisms [Harrington et al., 1999]. For example, degradation of glucose by Pseudomonas fluorescent is inhibited at a phenol concentration of 5.6 mg/l. At phenol concentration of 64 mg/l, inhibition of cell multiplication for Pseudomana starts [Verschueren, 1977]. The ability of microbial activity in degrading organic matter present in wastewater is inhibited by the presence of phenol as clearly demonstrated in Table 2.1.

Table 2.1 Effect of phenol on BOD [Verschueren, 1977].

<table>
<thead>
<tr>
<th>Time period (days)</th>
<th>BOD (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Original sample</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>13</td>
</tr>
<tr>
<td>15</td>
<td>14</td>
</tr>
<tr>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>25</td>
<td>16</td>
</tr>
<tr>
<td>30</td>
<td>16</td>
</tr>
</tbody>
</table>
BOD is a common method for the determination of organic matter in a sample. However, it should be noted that in the presence of toxins there is at times an inhibition of the bacterial activity which acts on oxidizing the biochemical organics in the wastewater. Such toxins are phenols, PAH and BETX [Abu Dahab, 1992]. This would furthermore explain the behaviour described in Table 2.1.
2.4 LOCAL, REGIONAL, AND INTERNATIONAL WATER QUALITY STANDARDS

Table 2.2 gives a comparative list of water quality discharge limits set by local, regional, and international authorities. The table includes phenol along with other water quality parameters. EPCL Refinery operates within the jurisdiction Jebel Ali Free Zone Authority (JAFZA) and therefore requires that the refinery meet all the regulation requirements as given in JAFZA promulgated regulations.

Table 2.2: Different effluent discharge regulatory standards from around the world.

<table>
<thead>
<tr>
<th>Parameter, mg/l unless specified</th>
<th>Dubai Municipality</th>
<th>JAFZA²</th>
<th>Oman (for agricultural or controlled aquifer recharge &amp; direct use)</th>
<th>Malaysian</th>
<th>Italy</th>
<th>France</th>
<th>Saudi Arabia (direct discharge)</th>
<th>Swiss</th>
<th>US EPA³</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>125</td>
<td>100</td>
<td>200</td>
<td>100</td>
<td>160</td>
<td>150</td>
<td>200</td>
<td>NA</td>
<td>21.3</td>
</tr>
<tr>
<td>BOD₅</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>50</td>
<td>40</td>
<td>30-40</td>
<td>30</td>
<td>30</td>
<td>4.25</td>
</tr>
<tr>
<td>Phenols</td>
<td>0.1</td>
<td>0.1</td>
<td>0.002</td>
<td>1</td>
<td>0.5</td>
<td>0.5-1</td>
<td>0.5</td>
<td>0.2</td>
<td>0.027</td>
</tr>
<tr>
<td>TSS</td>
<td>25</td>
<td>20</td>
<td>30</td>
<td>100</td>
<td>80</td>
<td>30</td>
<td>15</td>
<td>30</td>
<td>3.6</td>
</tr>
<tr>
<td>Oil and Grease</td>
<td>10</td>
<td>5</td>
<td>0.5</td>
<td>10</td>
<td>5-20</td>
<td>NA</td>
<td>10</td>
<td>20</td>
<td>1.3</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>75</td>
<td>50</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NA</td>
<td>15</td>
<td>NR</td>
<td>NA</td>
</tr>
<tr>
<td>Sulfides</td>
<td>0.1</td>
<td>0.05</td>
<td>0.1</td>
<td>0.5</td>
<td>1</td>
<td>NA</td>
<td>0.1</td>
<td>NR</td>
<td>0.024</td>
</tr>
<tr>
<td>Iron</td>
<td>2</td>
<td>0.3</td>
<td>5</td>
<td>5</td>
<td>2</td>
<td>NA</td>
<td>10</td>
<td>1</td>
<td>NA</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.1</td>
<td>0.1</td>
<td>5</td>
<td>1</td>
<td>0.5</td>
<td>NA</td>
<td>5</td>
<td>2</td>
<td>NA</td>
</tr>
<tr>
<td>Temp.(°C)</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>40</td>
<td>NR</td>
<td>By case</td>
<td>30</td>
<td>NA</td>
</tr>
<tr>
<td>TDS</td>
<td>NR</td>
<td>&lt;5000</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NA</td>
<td>NR</td>
<td>NR</td>
<td>NA</td>
</tr>
<tr>
<td>DO</td>
<td>NR</td>
<td>Min. 2</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>Min. 4</td>
<td>NR</td>
<td>NA</td>
</tr>
<tr>
<td>pH (unitless)</td>
<td>6-9</td>
<td>6.5-8.5</td>
<td>6-9</td>
<td>5.5-9</td>
<td>5.5-9</td>
<td>5.5-8.5</td>
<td>6-9</td>
<td>6.5-8.5</td>
<td>6-9</td>
</tr>
</tbody>
</table>

¹NR = Not Regulated, NA=Not applicable, NTU= Nephelometric Turbidity Units.
² JAFZA = Jebel Ali Free Zone Authority which is the local authority having environmental jurisdiction upon EPCL.
³ EPA specifies effluent limits and the limits vary from one industry to another, 30-day averages. The reference refers to EPA document EPA440/1-82/014 for discharge from petroleum refining industry. The limits are specified as per 1000 barrels of oil processed, [Nelson et al., 1991]
[Source: Various sources of water quality regulations through personnel communications with Refinery operatives, 2002]
The general effluent discharge regulations generally vary significantly between the different regulators in the world. These differences are possibility attributed to the foreseen further use of the effluents and/or the target environments in which the treated wastewaters are entering. For phenol, the maximum allowable concentration for discharge is 1 mg/l and that is generally to a long sea outfall. The JAFZA regulations which have jurisdiction over EPCL have dropped their standard from 0.5 to 0.1 mg/l for phenol. This has an impact on EPCL in encouraging more closely controlled operations to prevent pollution and exceeding this very stringent standard.

2.5 PHENOL IN CONDENSATE OIL REFINARY WASTEWATER

The formation of phenol in crude oil and condensates is based on different pre-processes that might have taken place. A common sense solution to pollution is to reduce the contaminant at the source itself. Thus, understanding the sources in which phenol evolves, may lead to better management and control of this chemical in treated wastewater. However, this may not always be possible especially at times when phenol is evolving from different sources and processes. It is both an engineering and feasibility call which may determine that after collection of the wastewater from various sources; an application of the waste reduction method should then be employed.

A major source of phenolic pollution comes from industrial sources. In oil refineries the typical range of phenol concentration in waste is 50 to 185 ppm for catalytic cracking wastewater to sour water streams, respectively [Abuzaid, 1995]. Similar levels of phenols in waste streams of a full fledged oil refinery have also been reported by Patterson [1998]. The author reported that the level of phenols typically falls in the range 80-185 ppm for raw outlets.
sour water, 40-80 ppm for general waste stream, about 80 ppm for post-stripping, 40-50 ppm for catalytic cracker, and 10-100 ppm for general wastewater.

A brief description of the culprit processes of few target waste steams of a condensate refinery (typical to the one under study) is given below. The target streams are those suspected to have appreciable levels of phenols. The processes upstream of the treatment plant will be discussed in light of process description and typical pollutant design loading. This section will further define the different ways that phenol finds its way in to the refinery wastewater, and these are discussed with respect to each suspected stream. The function of each operation is explained with reasons why and then an explanation to how the phenol actually becomes a contaminant in the wastewater being emitted from the following three sources in the refinery. The suspected streams given below are based on refinery operative discussions conducted at the start of this study.

2.5.1 Tank Water Drain (Tank-Water Draws)

The tank water draws are basically the removal of excess water which comes in contact with the condensate (crude) imported for processing. There is a limit made through the supply contract that limits the allowable water content for technical and financial reasons related to the supply contract. However, water can not be eliminated although the crude at source goes usually through a three-phase separator. However, even with that process emulsification is imminent. In addition to this, humidity and condensation in the cargo tanks during tanker transit is normal.

There are various pre-treatments which take place during the exploration processes where various chemicals are used for corrosion inhibition which may have an impact on the surfactant activity and this may have a great impact on the k-dissociation factors for the
phenols going from the water phase to the oil phase and vice versa. Furthermore, the use of chemicals to demulsify the water-oil mix in the upstream separators is also common in some exploration activities. These chemicals bear an impact upon the phenol in aqueous phase concentrations. Demulsifiers may have an impact and effects on the polarization of the components of pollutants in the water and oil.

The tank water draws at EPCL are a source of phenol and are very unpredictable in quality and pollution potential and loading on the wastewater treatment plant. The average phenol concentrations of water coming from the tank water draws are equal to 65 ppm. The COD values are very high indeed with values that range from 5,000 to 100,000 mg/l or even higher. The oil and grease levels range greatly between 6 to 125 ppm or even higher [personal communication with EPCL refinery operatives].

2.5.2 Desalter Wash Water

The deslating water wash is an integral step in any refinery for the removal of impurities from the crude before processing. Here the crude is physically washed with water and then passed across a two charged plate separator. The purpose of the desalter is to remove many of the impurities which are water soluble that come naturally in the crude and through the chemicals that are added to the exploration processes such as inhibitors and demulsifiers.

The desalter in EPCL is a 28 m³ vessel (3 m diameter and 4 m in depth) and typically has a flow equal to that of the refinery unit throughput. The desalted oil is taken to the process where it enters the condensate distillation column. A typical oil flow rate is between 300 and 450 m³/hr. The desalter is a vessel which has two charged plates operating at a voltage of approximately 365 volts and the washed crude water mix is passed through these plates in this
vessel. This is a continuous process and the retention time is approximately 4-5 minutes. Here the crude is washed and passes to the next section. Water that has to be introduced to this process is sweet utility water. The water is made available through injection and should constitute about 15-20% by volume of the crude inflow. Phenols can pass through into the crude and then into the fractionation process, but can also constitute some part of the ionic component of the water which is drained off from the desalter. The water is then routed to the effluent treatment plant.

The concentration of phenol in this water is a function of pH and temperature. As discussed earlier in this chapter, phenol has a high solubility in water which increases with temperature. From various long term data from the refinery, this stream was identified to contribute to phenol loading at the wastewater treatment plant. The level of phenol in this waste stream is highly dependant on the quality and characteristics of the crude oil itself.

The desalter wash water is made up of utility water and sour water stripper (SWS) wastewater. SWS wastewater is a product of any units that may potentially contain hydrogen sulphide (H₂S) and ammonia in the plant and may potentially contain significant phenol contamination. This may arise, for example, from the plant overhead drums, acid gas knock out drums, etc. The SWS wastewater is sent to the desalter where it is used as wash water. The stripped sour water is stored in the wash water drum and the difference of wash water is made up through topping up the storage wash water drum with plant utility water. Stripped sour wastewater is produced on an intermittent basis depending on the oil processing activities. There is one desalter for each CDU Plant with two CDU at the EPCL refinery.
2.5.3 MEROX Caustic-wash and Generation of Neutralized Spent Caustic Wastewater

The MEROX process is a trademark and patent process which was developed by UOP in the USA. Basically, once the products have been fractioned and separated using the distillation process in order to further ensure that the products are free of any impurities, the MEROX caustic wash process is employed.

The process is slightly different for kerosene (Jet-A1 fuel, used as aviation fuel), diesel (gas-oil), LPG and naphtha. The differences are in some preceding pre-wash steps and the concentration of caustic strength which is used in the different processes. Basically, the process requires that caustic is used in the washing of the petroleum product in a pretreatment vessel or in the MEROX vessel itself. The MEROX vessel contains a catalyst promoter in an activated charcoal bed with the product being mixed with the caustic and then air is injected into the vessel to speed the oxidation process. An oxidation reaction converts the mercaptan sulphur compounds into disulphide oils. Sodium mercaptides (R-S-NA+) and sodium phenolates (R-O-Na+) besides many other compounds are created.

The process caustic is then neutralized using sulphuric acid which is usually relatively strong. This creates reactions between the acids and produces phenols and may be other compounds as demonstrated in Fig. 2.6. This explains why the neutralized spent caustic which has to eventually be treated through the effluent treatment plant has a high degree of phenols as a waste stream. The products are then taken through a water-oil separation process using settlers, separators, salt and clay filters.
When Acid is added:

\[
\text{O-Na}^+ \xrightarrow{\text{NaOH}} \text{O-Na}^+ \quad \text{OH} \\
\xleftarrow{\text{H}^+} \\
\text{O-Na}^+ \xrightarrow{\text{HCl}} \text{O-Na}^+ + \text{NaCl}
\]

**Fig. 2.6:** Simple MEROX phenol neutralization reaction

The rate of generation and quality of the neutralized spent caustic at EPCL is very dependant on the type of crude being processed. Thus, the neutralized spent caustic is not only produced in a batch process, but with varying pollution potential and volumes. Hydrogen peroxide is added at times to this waste stream to try to reduce the COD and phenol level and carbon dioxide is bubbled through it to control the pH.

### 2.5.4 Methods Employed for Treatment of Wastewater Containing Phenol

Industrial wastewaters originating from oil production processes, especially those coming from the production processes contain phenols in high concentrations (>10 g/l) [González et al., 2001]. Treatment processes which use adsorption with bone char or zeolites, stripping with air or stream, wet air oxidation, trickling filter, oxidation ponds, lagoons and use of pure or mixed culture of micro-organisms are examples of several physio-chemical and biological treatments techniques used to remove these toxic compounds.
Refinery wastewater having low phenol concentration in the range 5-500 ppm is suitable for biological treatment. The efficiency of biological methods employed for the treatment of phenol-contaminated wastewater varies with operating process variables such as pH, temperature, dissolved oxygen, nutrients containing phosphorus, nitrogen and minerals [Abuzaid, 1995].

Sokó [1998] used a continuous stirred tank as a bioreactor to degrade phenol by *Pseudomonas putida* (Pp) strain-type bacteria. At a temperature of 30°C and with the pH maintained at 6.8, the specific uptake rate calculated from a kinetic model was adequate and complementary to the experimental data in transient states. Annadurai et al., [2002] used the previous strain of bacteria (Pp), activated sludge and mixed liquors of two different biomass samples to investigate the biodegradation kinetics of phenol as a function of different factors. The results demonstrated that the highest degradation of phenol for all types of biomass took place at an initial concentration of 100 ppm with a removal of 60-80%, whereas the lowest was at 500 ppm (30-58%). Moreover, mixed liquors of the two types of biomass have higher phenol reduction than individual systems. The maximum degradation (80%) occurs within a pH range 6.8-7.2, temperature range 30-30.6°C and at concentrations equal to 0.5 g/l for both glucose and (NH₄)₂SO₄. The reaction was found to have a second-order polynomial regression which was used based on the interpretation of the experimental data [Annadurai et al., 2002].

Onysko et al., [2002] studied the (Pp) strain-type bacteria which were used again to degrade phenol under unsteady state conditions of immobilized cell fluidized bed reactor (ICFBR). The authors developed a new dynamic model to simulate the response of all four key process variables: bulk phenol concentration, suspended biomass concentration, concentration of substrate and the biofilm thickness.
Through using a pure culture of immobilized cells of the \((Pp)\) strain-type bacteria a study of the biodegradation of phenolic industrial wastewater in batch and continuous systems was conducted by González et al. [2001]. The experiments were conducted aerobically at temperature of 30°C and pH of 6.6. The initial phenol concentration in the two systems (i.e., batch and continuous ones) ranged between 200-1000 ppm and 250-500 ppm, respectively. Phenol was degraded completely in every batch experiment, whereas degradation reached only 90% in the fluidized bed reactor. Here also 75% of the non-phenolic compounds present in wastewater were degraded.

Alemzadeh et al. [2002] studied the removal of phenol by \textit{Rhodotorula glutinis} in a three stage cross flow rotating biological contactor (RBC) with 24 discs. Under anaerobic conditions, the removal efficiency of 99.9% was observed at temperatures of about 36°C and loading of \(4 \times 10^3\) m\(^3\)/m\(^2\) per day and COD concentration of 800 mg/l. Three removal mechanisms were observed; biodegradation, surface adsorption and evaporation. A strain of \textit{Rhodococcus erythropolis} had been isolated and identified by an RNA sequencer. Immobilization of cells on ceramic support of “Biolite” resulted in a remarkable enhancement of the respiratory activity of cells and a shorter lag phase preceding the active phenol degradation. When using wastewaters of local plants containing both formaldehyde and phenol, the immobilized cells were able to remove completely the first compound and partly biodegrade the second one at rate of 1 kg phenol/m\(^3\).d.

In a study by Klimenko et al. [2002], activated carbon had been considered as a carrier of \textit{Pseudomonas} biofilm only. The impact of the physico-chemical factors such as the change of free energy \((-\Delta G^\circ)\) and the porous structure of the activated carbon on the effectiveness of
the biosorption process has been established. The relationship between biological degradation into the biosorption process and the free energy $-\Delta G^\circ$, was inversely proportional. Finally, the micropores of the active carbon are occupied by adsorption molecules and are not subjected to biological regeneration.

Sequential anaerobic-aerobic processes have been used by Shin et al. [1999] to degrade 4-CP and 2,4-dichlorophenol (2,4-DCP). Scraped vehicle tires were used as packing material with adsorption capacity equal to a range of 0.04 to 0.3% of that of the activated carbon. The biofilm was used with the tire chips. It was found that 2,4-DCP was completely degraded in an anaerobic biofilm reactor and 70% of 4-CP was removed in the subsequent aerobic biofilm packed with tire chips. Moreover, an anaerobic-aerobic biofilm reactor could be used for complete mineralization of polychlorinated compounds.

Phenol biodegradation had also been studied in batch experiments with an initial phenol concentration ranging from 100 to 1300 mg/l. The inhibitory nature of phenol at high concentrations was described and considered within the growth rate [Goudar et al., 2000]. Both Pseudomonas putida and Trichosporon cutaneum strains were used. No phenol degradation was observed for phenol concentrations greater than 1300 mg/l. A lag phase of six hours were needed for the acclimated microbial culture to reach an initial phenol concentration equal to 200 mg/l, whereas it took 20 hours to reach the same phase at 1300 mg/l phenol. Non-viable pre-treated cells of Aspergillus niger were used to remove phenol in trace quantities which was usually present in the treated effluent of many wastewaters [Rao and Viraraghavan, 2002].

In conclusion, there have been many studies undertaken on the different types of bacteria and systems used for the control of phenol and other pollutants. The complexity that the research has identified lies in the great number of variable parameters that exist in such experiments.
including the physical, chemical and biological factors. Still the challenge is great as many variables exist and in any study the prevailing site conditions may have a bearing and should be carefully addressed.
CHAPTER THREE

THE ENOC REFINERY AND EFFLUENT PLANT PROCESS DESCRIPTION

3.1 EMIRATES NATIONAL OIL COMPANY (ENOC) AND EPCL REFINERY

The ENOC was formulated eleven years ago in 1993 from various companies which were operating within the oil and gas sector and mainly in the services and marketing sectors of the industry. Such companies like Emirates Petroleum Products Company (Eppco), Cylingas Company Ltd, Emirates Gas LLC, ENOC (Chemical) Terminals Ltd and some others that followed from 1993 until 1998 when the ENOC Processing Company Ltd (EPCL) was formulated and work started on the design. In fact to date some 28 companies are registered under the ENOC Group of Companies. ENOC continues to expand not only within the UAE but has in more recent years started tapping into the world markets and international operations. The EPCL plant itself is located in the north side of the Jebel Ali Free Zone Area, which is about 30 km from the centre of the Dubai emirate in the UAE. The plant is within the hydrocarbon processing, handling and storage zone within the free zone master zone plan.

The EPCL is the first oil refinery in the Dubai Emirate in the UAE and was designed based on the International Oil & Gas Engineering Standards. The Front End Engineering Design (FEED) was completed by M W Kellog and the construction was done by the Italian based company Technip, which was previously known as Technipetrol. Some of this information is available in the ENOC Company Website [ENOC, 2003].

At the same time an environmental impact (EIA) and risk assessment (RA) project was undertaken and the assessment of environmental impacts were identified with the assistance of external consulting engineers as the management of ENOC felt it important to evaluate such impacts in line with the Jebel Ali Free Zone Authority environmental rules and regulations. This EIA study was later
also complemented by a two-stage environmental impact assessment of the effluent discharges which was undertaken by two separate environmental consultants, and these studies were at the request of the regulator. The studies also collected data on the harbour water quality to establish a benchmark and to also later assist in the definition of impacts.

The EPCL is a 120,000 barrels per stream day condensate splitter refinery with various plants including MEROX sulphur removal units, sulphur recovery plant, power & utilities plant, crude and product storage tank farms, LPG spheres, a cooling tower plant all with their respective accessories of pumps and other auxiliary equipment. Another very important plant which is the focus of this thesis study is the effluent treatment plant (ETP) which since it was been commissioned has been upgraded to meet new regulations.

Due to the nature of condensate, the plant has little environmental emissions when compared to other more complex crude oil refineries which have other units such as hydro-crackers, vacuum distillation units and coking units which have significant environmental impacts related to their operations. However, also due to the nature of the oil business, the crude condensate oil received by the refinery are at times varying in basic quality and with the use of injection anti-corrosion inhibitor chemicals and different drilling muds, the quality is not always consistent.

This is in fact why it becomes difficult at times to process the crude as well as the wastewater effluents which are generated from the different processes in the plants within the refinery such as primarily the de-salters and the MEROX units.

The EPCL consists of 2 main processing plants with 60,000 BPSD condensate splitters each and a further smaller naphtha splitter in each plant. Downstream processing continues with sulphur removal using a UOP patent technology called the MEROX units which are a basic type of caustic wash for the products.
This study is concerned with the operation of the effluent treatment plant and reviews the data since its commissioning to see what are the main factors affecting the quality of the effluent at different modes of operation specifically with respect to phenol removal.

3.2  ENOC PROCESSING COMPANY LLC ETP

3.2.1  General Process Description

The ETP receives all the effluent coming in from all parts of the Refinery into a centralized diversion box which is a large capacity holding compartment. These streams include a total of 18 main streams that include:

1. Wet Slop which is recycled through the wet slop sewerage system - back to the crude tanks.
2. Sour-water-stripper bottoms
3. Desalter effluent
4. Boiler blow-down
5. Cooling water blow-down
6. Utility water caustic soda pumps flushing
7. LPG vaporizer polluted condensate
8. Fuel oil heater polluted condensate
9. MEROX plants caustic soda
10. Caustic heater condensate
11. Pre-treated neutralized spent caustics wastewater
12. Oily water from MEROX plants
13. Pad drainage and storm water run-off
14. Naphthenic neutralized spent caustic wastewaters
15. Crude Condensate tank drain water (tank water drains)
16. Storage area storm water
17. Clean storm water which goes directly to the discharge point if deemed clean from paved and process areas (Pad-runoff)
18. Sanitary wastes which go directly to the sand drying beds and the water is returned to the surge pond which later on goes into the treatment, outside the scope of this study.

It is important to note that the refinery processes are extremely complex and that the flowing streams come with different constituents and different flow rates. The flows described in Table 3.1 below are only indicative and give just an indication based on the material balance calculations that were taken initially by the plant designer. Actual flows from data collected directly from plant operatives are given in Table 3.2.

3.2.2 General ETP Process Description

The contents of the compartment can be sent either into the processing of oil removal using the corrugated plate induced (CPI) separators or other which to an open and large capacity holding basin known as the surge pond. After having the floatable and emersed oils removed through this physical separation process, the effluent enters another stage of treatment using the induced gas flotation (IGF) physiochemical process which uses a polymer injection and air injection to remove further the oil content.

After the IGF process the effluent is used to fill a SBR which uses biological activated microorganisms in cyclic processes to consume the remainder of oil and other effluent constituents in a biological process. There are other aspects of this process which will be discussed in the next section. The SBR has to be decanted and this is done into an underflow, then over flow weir arrangement in order to remove the floatable and suspended solids from the effluent.
which is by this point relatively clean. This is done before the effluent is pumped through a sand filter which helps in removing the suspended solids producing a clearer liquid. The outlet flows from the sand filter are passed through a carbon (charcoal) reactor which aims at removing the dissolved solids and pollutants by adsorption processes. The effluent is then sent to a final storage pond before it is discharged into the harbour waters.

3.2.3 Process Flow Diagrams

A basic descriptive process (schematic) flow diagram of the process that is considered in this study is shown in Fig. 3.1. The flows and the typical pollutant loadings as per the plant design are given in Table 3.1 below. Refer to Appendix 1 for a full schematic diagram [P&ID Drawing Reference: 22-A-10001 Rev. 6 of the effluent treatment plant].

![Process Flow Diagram](image)

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Fig. 3.1: Process flow diagram extract for the ETP (adapted from EPCL, 2002).
Table 3.1: Typical details of different key inlet streams to the ETP [EPCL, 2002]

<table>
<thead>
<tr>
<th>Stream No.</th>
<th>Stream title</th>
<th>Design hydraulic rate (m³/hr)</th>
<th>pH</th>
<th>BODs (mg/l)</th>
<th>COD (mg/l)</th>
<th>O&amp;G (mg/l)</th>
<th>TSS (mg/l)</th>
<th>TDS (mg/l)</th>
<th>Phenols (mg/l)</th>
<th>Sulphides (mg/l)</th>
<th>Temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Desalter O/L</td>
<td>23.5</td>
<td>7.9</td>
<td>500</td>
<td>850</td>
<td>200</td>
<td>100</td>
<td>2000</td>
<td>10</td>
<td>5</td>
<td>41</td>
</tr>
<tr>
<td>2</td>
<td>Tank drain water</td>
<td>10</td>
<td>7.9</td>
<td>500</td>
<td>850</td>
<td>10,000</td>
<td>100</td>
<td>2000</td>
<td>10</td>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>Neutralized spent caustic¹</td>
<td>0.41</td>
<td>7.4</td>
<td>675</td>
<td>19606</td>
<td>112</td>
<td>18.9</td>
<td>138818</td>
<td>238.2</td>
<td>53</td>
<td>40.8</td>
</tr>
<tr>
<td>4</td>
<td>I/L CPI Separator</td>
<td>42.4</td>
<td>7.9</td>
<td>277</td>
<td>469</td>
<td>169</td>
<td>35</td>
<td>6402</td>
<td>20</td>
<td>6</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>I/L IGF Unit</td>
<td>42.4</td>
<td>7.9</td>
<td>277</td>
<td>469</td>
<td>30</td>
<td>10</td>
<td>6402</td>
<td>20</td>
<td>6</td>
<td>41</td>
</tr>
<tr>
<td>6</td>
<td>O/L IGF Unit</td>
<td>45</td>
<td>7.9</td>
<td>277</td>
<td>900</td>
<td>30</td>
<td>10</td>
<td>6402</td>
<td>20</td>
<td>6</td>
<td>41</td>
</tr>
<tr>
<td>7</td>
<td>O/L SBR-B</td>
<td>45.4</td>
<td>6.9</td>
<td>30</td>
<td>150</td>
<td>10</td>
<td>10</td>
<td>6402</td>
<td>0.5</td>
<td>0.1</td>
<td>35</td>
</tr>
<tr>
<td>8</td>
<td>O/L SBR-C</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
</tr>
<tr>
<td>9</td>
<td>O/L Sand filter</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
</tr>
<tr>
<td>10</td>
<td>O/L Carbon bed reactor</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
<td>NDA</td>
</tr>
<tr>
<td>11</td>
<td>Final effluent pond</td>
<td>60</td>
<td>6.5-8.5</td>
<td>20</td>
<td>120</td>
<td>5</td>
<td>20</td>
<td>&gt;5000</td>
<td>0.1</td>
<td>0.1</td>
<td>35</td>
</tr>
</tbody>
</table>

¹ This stream is a mass-flow ratio figures represented for the design process flow diagram basis and the flow rates into the plant are based on the operations at the time from the neutralized spent caustic storage holding/tank. It gives a basic idea of the typical-design based quality.

² Streams 8, 9 and 10 do not have design basis flows/qualities data on the refinery drawing.
Table 3.2: Details of typical actual flow rates, range of retention times, basic operating volumes and process type classification for the ETP.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Basic function</th>
<th>Typical range of retention time (hr)</th>
<th>Flow rate (m³/hr)</th>
<th>Basic operating volume (m³)</th>
<th>Process type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diversion box</td>
<td>Initial effluent receipt point</td>
<td>0.5</td>
<td>20-30</td>
<td>13.25</td>
<td>Continuous</td>
</tr>
<tr>
<td>Surge pond</td>
<td>Overflow storage pond</td>
<td>Variable</td>
<td>Variable</td>
<td>1271.51</td>
<td>Semi Continuous</td>
</tr>
<tr>
<td>CPI separators</td>
<td>Floatable oil and dirt removal</td>
<td>1</td>
<td>25-30</td>
<td>29.39</td>
<td>Continuous</td>
</tr>
<tr>
<td>IGF</td>
<td>Floatable and emulsified oil removal</td>
<td>0.3</td>
<td>25-30</td>
<td>9.38</td>
<td>Continuous</td>
</tr>
<tr>
<td>SBRs</td>
<td>Emulsified oil and organic/inorganic waste reduction</td>
<td>23</td>
<td>40</td>
<td>921.7</td>
<td>Batch</td>
</tr>
<tr>
<td>Overflow/Underflow Weir = Skimming Basin</td>
<td>Removal of floatable and settable debris</td>
<td>8</td>
<td>NA</td>
<td>841 / 2490</td>
<td>Semi Continuous</td>
</tr>
<tr>
<td>Sand filters</td>
<td>Removal of suspended matter</td>
<td>0.5</td>
<td>35</td>
<td>16.3</td>
<td>Semi Continuous</td>
</tr>
<tr>
<td>Carbon Bed</td>
<td>Removal of dissolved organic matter</td>
<td>1</td>
<td>35</td>
<td>38.9</td>
<td>Semi Continuous</td>
</tr>
<tr>
<td>Final effluent ponds</td>
<td>Storage of final effluent</td>
<td>8</td>
<td>-</td>
<td>674.3</td>
<td>Batch</td>
</tr>
</tbody>
</table>

NA=Not Available

The values given in Table 3.2 are based on information obtained from refinery process engineering operatives. The typical retention times are based purely on information obtained from operators in the ETP. The flow rates are generally lower than the design flow rates in a typical operation and the basic operating volume and process type is based on design data.
3.3 EFFLUENT TREATMENT PLANT UNITS DESCRIPTION

3.3.1 Diversion Box

The diversion box serves the dual function of (1) serving as the lift station for transfer of the normal dry weather oily water sewer (OWS) flows to the ETP, and (2) for diverting the first flush wet weather flows from the process and utility areas to the process water surge pond. Wet weather flows in excess of the first flush volume will be released from the diversion box to the storm water sewer (SWS). The diversion box is a field constructed, in ground concrete structure. The box is partitioned into two sections by means of an overflow weir: an inlet section into which the OWS drains and which houses the two vertical CPI separator feed pumps and, downstream of the overflow weir, an outlet section which preferentially drains to the process water surge pond which is described in the next section. The outlet section is also provided with an overflow line which drains to the SWS. A trash rack is provided upstream of the pumps and a manually operated sluice gate is provided on the outlet line which drains to the process water surge pond.

The inlet section of the diversion box is completely enclosed. This is accomplished by covering the section with a vapour tight roof and by providing a liquid seal underflow baffle upstream of the overflow weir. Initially, the inlet section will be vented to the atmosphere and or in case of a serious odour problem is experienced with the atmospheric vent, it may be necessary to route the off-gases through a control device. The outlet section of the diversion box is covered with grating. The outlet section, which drains to open structures (the process water surge pond) need not be enclosed with a vapour tight cover.

In operations the dry and wet weather flows collected by the OWS gravity drain into the
inlet section of the diversion box. The normal dry weather flows are transferred to the CPI separators by means of the CPI separator feed pumps. Of the two pumps, provided, one serves as a full capacity spare.

The wet weather flows in excess of the capacity of the transfer pumps will overflow the internal weir into the outlet compartment which preferentially drains through an interconnecting sewer line to the process water surge pond. Should the pond become full, any additional wet weather flows will be released to the storm water sewers by means of the gravity-flow overflow line. Should it be necessary to take the process water surge pond out of service for maintenance, cleanout or inspection, the pond can be isolated from the diversion box by closing the sluice gate. The CPI separator feed pumps will be operated on on/off level control. The diversion box will be equipped with a high level control for notification of overflow to the SWS. The diversion box shown in Fig. 3.3 is a rectangular, partially enclosed, in ground, concrete structure partitioned into two sections by means of an overflow weir with a maximum peak flow rate of 18.6 m³/h. The average flow into the box is about 6 m³/h and the wet weather design is about 1,178 m³/h. The sketch below (Fig. 3.2) shows the engineering of this diversion box.
Fig. 3.2: Diagram-type sketch of the Diversion Box [Kellog, 1997]

Fig. 3.3: Photograph of the Diversion box with the surge pond behind it. There are some different pumps used for the transfer of the raw effluent into the CPI separator and the surge pond as deemed necessary by the operators. The two erect grey pipes are vent pipes to release the build up of fumes from the oily water being stored in the diversion box.
3.3.2 Surge Pond

This is a lined concrete with high density polyethylene (HDPE, 1.5 mm thick) liner and construction 1,400 m³ capacity holding basin constructed at 1:3 vertical to horizontal slopes with a composite membrane-clay liner system meant for use for excessively polluted waters or at times where the effluent is very high in quantities in order to preserve the operations of the ETP including first wash in the wet weather conditions. It receives all the effluent coming from all 15 streams in the refinery through the transfers that it receives from the diversion box. It also receives the sand and carbon filters backwash water and the water that percolates from the sand drying beds described in later sections. The Surge pond can be said to also act as an interim stabilization or dilution pond that will most probably have the typical average inflow characteristics of the raw effluent. The pond is served by process flow transfer pumps which are housed in the pond and an oil skimmer package for the removal of excess waste oils.

The operating description is such that excess rain weather flows and firewater runoff from the battery limits of the process and utility areas drains from the outlet section of the diversion box to the process surge pond. From the pond, the collected runoff will normally be transferred to the CPI separators at a gradual rate by means of the transfer pumps. An alternate routing from the pump discharge line to the storm water sewer is provided should the collected water be acceptable for discharge without any further treatment. Free oil which may accumulate on the pond's surface would be recovered by means of the oil skimmer package. Figures 3.4 and 3.5 show the sketch and photograph of the process water surge pond respectively.
Fig. 3.4: Diagram type sketch of the Process Water Surge Pond [Kellog, 1997].
3.3.3 **Corrugated Plate Induced Separator (CPI)**

This is the first treatment step in the ETP. The function of the CPI is a continuous operation which is based on the removal of floatable oil by using plates which are shallow settling devices consisting of stacked offset trays of various geometric shapes. The plates enhance the removal of the oils by coagulating the oil partials which enter the separator as an emulsion. As the partials adhere and join one another they are greater in size and more readily float to the surface where they are skimmed using tube like skimmers. The sludges which are a combination of very heavy oils, dust, particulates and other types of objects such as debris fall to the bottom where they are removed and drawn in to a sludge pit which is periodically cleaned.

To help keep the plates clean they are usually inclined at an angle of about 45 degrees. This also ensures the removal of floatable oils and sludges as described efficiently. The CPI separators are in a sealed vessel in the interest of reducing the odour that may arise from this process as is the case with refineries that use API separators which are open channels and have a different mechanism of operation.

Plate and tube settlers have been developed on the basis of the practical limitations of producing very shallow basins. Plate and tube settlers consist of stacked off-set trays or bundles...
of small plastic tubes of various geometries. Although tube settlers have been used in primary, secondary and tertiary sedimentation applications, a number of problems have developed with their use. The primary problem is the clogging and odours due to the biological growths and the build up of dirt-mixed greases. Again for self cleaning the inclination of the plate should be anywhere between 45 to 60 degrees [Reynolds and Richards, 1996].

They are used in conjunction with both existing and specially designed sedimentation basins. Figure 3.6 below shows some photograph of these separators.

![Photographs (side and front views) of the two 100% CPI separator units.](image)

**3.3.4 Induced Gas Flotation Unit (IGF)**

This is a small unit with a typical flow rate of 39.7 m³/h and operates on the principle of gravity and density differences. Using a specific polymer known as a polyelectrolyte/strong cationic additive with trade name NALCO-71454 which consists of water, the polymer and inorganic salts with a boiling point of approximately 130°C and a pH 4 it is added at a certain concentration and injection rate. The polymer is injected and also air is supplied to bubble through which removes both floatable and some of the emulsified oils from the wastewater. Typically this process is employed to reduce the oil content as per design from some 30 ppm to about 20 ppm for both free and emulsified oils. The removed oil is sent to the oily sludge sump which it shares with the CPI units. It by design has little if any impact on the reduction of phenols.
The purpose of the IGF units is the removal of residual emulsified and colloidal oil and suspended solids which were not removed in the upstream CPI separators unit operations. This is accomplished through the addition of a chemical polymer for the destabilization of the suspended particles, and the introduction of extremely small gas bubbles which, through adherence to the destabilized and agglomerated particles, enhance their natural gravity separation from the bulk water phase. The flotation medium for the IGF unit will initially be air, although provisions are allowed for the future substitution of an alternate flotation medium such as nitrogen.

Effluent water from the CPI separators gravity flows to the IGF unit tank. The polymer is injected into the combined CPI effluent stream upstream of an in-line static mixer which serves to ensure adequate chemical dispersion. The chemically conditioned process wastewater is then introduced into the IGF flotation tank. The tank is divided into five compartments by means of internal weirs: four flotation cells and one effluent clear-well. In each of the flotation cells, a mixture of recycled wastewater and flotation gas is introduced into the raw wastewater through distributors. The released gas bubbles adhere to the destabilized solids, carrying the suspended matter to the liquid surface from which the float is skimmed to an internal compartment. From the compartment, the float material is transferred by means of the IGF float pumps to the condensate feed tanks via the slop oil header for recycling.

Flotation gas is continuously circulated from the vapour space of the flotation cell to the internal cell distributors. Circulation is accomplished by educting the flotation gas into a circulation stream of treated IGF effluent. The IGF recycle pumps take suction on the effluent compartment of the flotation tank and discharge through eductors into the cell distributors. A net gas makeup is generally maintained at all times to purge the flotation tank of light hydrocarbons. The vent gas from the unit is released to the atmosphere. The treated IGF effluent is pumped to the downstream SBRs by the IGF effluent pumps. It is important to note that the pH is controlled in this process to 7-9 to achieve proper
operation of the biological system downstream. It is expected that the combined wastewater stream will routinely be in the required pH range and will not require any adjustment. However, the transfer piping has been fitted with a tie-in connection to dose with acid or caustic to ensure in addition to a spool piece to provide a mixer on the line should it be required. Figure 3.7 below shows the different parts of the IG unit.

![Figure 3.7: The IGF system unit (LHS), polymer drum and dosing pumps (RHS), and IGF unit side view showing the five compartments and bottom frame showing the associated pumps.](image)

### 3.3.5 Sequencing Batch Reactors (SBR)

The SBR is a fill-and-draw type reactor system involving a single complete-mix reactor in which all the sets of the activated sludge process occur. Mixed liquor remains in the reactor during all cycles, thereby eliminating the need for separate secondary sedimentation tanks. Therefore, the unit operations and processes that are involved in an SBR and conventional activated sludge system are identical, because the sedimentation and clarification are carried out in both systems. However, there is one important difference and that is in conventional
plants, the processes are carried out simultaneously in separate tanks, whereas in the SBR it all takes place sequentially in the same tank. This is better explained below.

The SBR system is a batch operated biological system. The primary function of the biological treatment is the removal of soluble biodegradable organics, with the removal or residual insoluble organic and inorganic suspended matter being a secondary, yet incidental, consequence. The removal of the soluble bridgeable organics is accomplished through the metabolic activities of a mixed culture of micro-organisms. The organisms of importance to water treatment are bacteria which utilize organic substrate as the energy source necessary to sustain the basic metabolic functions as well as for the synthesis of new microbial cells. The removal of suspended organic and inorganic matter primary occurs due to enmeshment in the bio-flocs.

**Aerobic Digestion:** Aerobic digestion is an alternative method of treating the organic sludges produced from various operations. Aerobic digesters may be used to treat mixtures of waste-activated sludges. This takes place in the SBR and the feedstock for the bacteria is the oils within the refinery wastewater system. The SBR system is an extended aeration, completely mixed activated sludge biological treatment unit operated in a true batch mode. To allow for continuous operations, the system includes more than one reactor.

Each of the four reactors currently installed operates on a PLC controlled sequence of operations during each batch cycle. A complete cycle includes the following operating periods:

1. **Anoxic Fill Period:** The reactor is nearly filled with wastewater, typically to some 8.5 meters from the bottom of the tank (tank height total = 10 m) in the presence of pre-settled activated sludge but in the absence of supplied aeration. The purpose of the fill operations is to add the substrate (raw wastewater) to the reactor. The fill process typically allows the liquid level of the reactor to rise to at least 25% of its capacity. The blowers are not operated during this fill period for operational reasons.
2. Aerated Fill Period: The reactor is filled to its operating capacity with the initiation of aeration. So the filling of that tank takes place in both the anoxic followed by aerated operations during the filling phase. Both these phases take about 25% of the total cycle time.

3. Reaction Period: Once the reactor is full and the wastewater feed diverted, the reactor enters into a period of aeration during which the micro-organisms consume the soluble organic substrate. This stage takes a minimum of 35% of the total cycle time. However, with higher pollution loading this reaction time is extended significantly under refinery wastewater treatment plant operations.

4. Quiescent Settling Period: During this period the purpose is to allow the solids separation to occur and the biomass to settle to the bottom of the tank. With this a clarified supernatant to be discharged as effluent. In an SBR, this process is normally much more efficient than in a continuous flow system because in the settle mode the reactor contents are completely quiescent.

5. Decant or Draw Period: Following the settling of the biomass, the clarified treated wastewater is decanted from the upper portion of the tank and discharged. The reactor is now ready to again receive feed wastewater and repeat the batch cycle. In decanting generally there are various methods that may be employed with the most popular being used in EPCL which is the floating or adjustable weirs decanting arm. The tank draw may take anywhere between 5 to 30% of the batch cycle, but generally takes about 1 hour in EPCL.

6. Idle Phase: The purpose of the idle in a multi-tank system is to provide time for one reactor to complete its fill cycle before switching to another unit. Because idle is not a necessary phase, it is at times omitted. In EPCL with the installation of 4 batch reactors, there is flexibility with processing wastewater and at times a SBR will be left for a few hours on a decant mode [Reynolds et al, 1996].
Proper aeration of any biological treatment units requires that the wastewater feed include a sufficient amount of nutrients, principally ammonia and phosphorus, to support the metabolic activities of the organisms. While the process wastewater is expected to contain a sufficient amount of ammonia, it is likely to be deficient in phosphorus. Consequently, a packaged phosphoric acid injection system is also included in the SBR package described above. Should ammonia be needed at any time, urea pellets are added from the top of the open tank during the mixing phases as well. Periodically, excess sludge generated in the process is drawn off from the tank and transferred to the sand drying beds. Their operations are described in the section below.

The neutralized spent caustic wastewater (referred to in Chapter 2) which is one of the most troublesome streams has been stored in a dedicated tank which was built in the ETP about two years after the refinery started its operations. It is important to make a note of this as this effluent is stored and fed slowly to the SBR inlet with the IGF outlet effluent to two out of the four SBRs, SBR-C and SBR-D and from more recent communications with the refinery operatives SBR-A.

The bacteria in these two or now three dedicated SBR units have been acclimatized through a long process of slow concentration increases in feed to deal with high COD and phenol effluents. This method which was implemented by the engineering and operations department in the refinery helped deal with this very serious and challenging problem to ETP continuity.

It is worthy to note that the initial plant design was purely for the installation of 2 SBR units only and was further developed and 2 more unit tanks were installed two years after the first oil-in operation in the refinery. This was with the addition of the tertiary treatment facilities as discussed below.

It is further worthy to note that during the period of this study, the refinery dedicated SBR C to the consumption of some 1 part neutralized spent caustic to 35 parts IGF effluent.
The SBR B, however, is dedicated until recently to effluents from the IGF directly and only. This explains the basic challenge that faced in the testing and it is reflected in the conclusions we have come to in testing. Figure 3.8 shows a photograph of SBR-B.

![SBR-B Tank](image)

**Fig. 3.8**: The SBR tank which is 10 m deep with a diameter of approximately 8 m.

### 3.3.6 Sand Drying Beds

Excess waste activated sludge from the SBR and the sanitary waste treatment package (which is outside the scope of this study) will be dewatered on the three identically designed sand drying beds. Following dewatering, the residual solids will be transferred to a truck for off-site disposal to a landfill.

The sludge dewatering system consists of three open sand drying beds, 6 m wide by 22 m long constructed with a 450 to 525 mm deep fill of graded sand and gravel plus an under drain leachate collection system. The general layout and design of the drying beds is presented in the Fig. 3.9 below.
The system is operated when the waste activated sludge from the SBR and the sanitary waste biological treatment package discharge onto the sand drying beds on a periodic basis. Multiple beds are provided so that as one bed is in the fill mode, the other beds can be in the drying mode. Dewatering occurs through a combination of percolation and evaporation, with percolation accounting for approximately 20-55% of the water removal. The beds are provided with an underdrain leachate collection system consisting of perforated pipes. The under drain system drains to the leachate sump, from which it is returned to the SBR by the leachate sump pumps. Once the sludge is dewatered to a lift able state, the residual material will be transferred to trucks for off site disposal. Sludge removal can be by manual shovelling or by means of a front-end loader.
The drained water is collected by the underdrain system which drains to the leachate sump. From the sump, the water is returned to the SBR by the leachate sump pumps. The pumps in fact of which one is a full capacity spare operate on an auto-mode on/off sump level controller. Typical pH value at 25°C using the APHA 4500-H+ after extraction is 6.9, oil and grease (APHA 5520 method) equivalent to 0.36% by weight and moisture content (gravimetry) equal to 12.2. All metals are less than 1% by weight generally except for iron which is typically much higher. This is based on refinery discussions and waste management records. A photograph of the sand drying beds is given in Fig. 3.10.

![Fig. 3.10: The sand drying beds which are emptied on average once every 90-100 days of operation and the high temperatures in Dubai assist in the dewatering process. Normal desert sand is used as the substrate material after filling.](image)

### 3.3.7 Underflow/Overflow Weir (Skimming Basin) Pond

The supernatant liquid which is decanted from the SBR is usually relatively clean, but there are some floatable materials which pass with this liquid during decanting. It was observed during the first year of operation in the plant that it would be difficult to cure this problem at the decant phase and therefore this overflow, underflow weir pond system was designed and constructed. The operation is quite simple and straightforward. There is an overflow
weir system which removes all settleable material which passes through from the SBR. This material is settled out. Then an underflow system tries to remove the floatable suspended material which passes through the system.

Although the initial design did not foresee this, after operating the plant for nearly two years this system was implemented and has assisted greatly with the alleviation of the problem of suspended and settable particles. It is very important to note that it was also a very necessary process to include prior to the sand filters and carbon reactors which are installed downstream of the SBR process. In Fig. 3.11 the photograph of the skimming basin shows the longitudinal view of the basin.

There is also a skimming system which is employed which removes the floatable material which with the direct sunlight on the basins surface is algal growth. There is a growth control system employed based on chemical inhibitor addition to this system to control this natural problem.

Fig. 3.11: Photograph of the continuous flow operations in the over/underflow weir system-Skimming Basin. There is algal growth formation at the top of the pond due to the favourable conditions of the nutrient rich supernatant liquid with passes through the system. This is with a basic boom-type skimmer system which is operated to remove floatable material periodically. The rope that can be seen is the basic tracker for the skimming boom.
Again in line with the aim to implement tertiary treatment, the sand filters are the second stage of treatment in which the removal of fine particles by filtration is accomplished. From the overflow/underflow weir or skimming basin, the effluent is pumped to the sand filters. The operating philosophy of the sand filters is "one on line, and one on stand by", thereby ensuring that the wastewater will always pass through one filter and giving the other a chance to be backwashed. The sand filter has been proven to help remove the finer particulates that could not be removed by skimming basin operations. By carrying out this function, the sand filter will help enhance the performance, and extend the life of the downstream carbon filters. Both sand filters have been provided with automatic back-washing and air scouring facilities. Figure 3.12 shows the two sand filter vessels used in the ETP whereas the sand quartz material used in the filter is shown in Fig. 3.13.

Fig. 3.12: Two 100% sand filter units which work on an alternate basis. Whilst one is in the filtering process the other is being backwashed to prepare it for the next batch. The pressure differential is monitored both automatically and manually in the system.
3.3.9 Activated Carbon Reactors

After all the solid matter has been removed from the effluent stream, it is then passed onto the next stage of treatment which is the carbon reactor. Figure 3.14 shows the carbon material used in the carbon bed. In a similar manner to the operating philosophy of the sand filter, the carbon reactor is “one on line and the other on stand-by or backwash mode”. The carbon reactors are to have a specially selected coal based filtering medium. The filter medium was selected on a basis of high surface area, and high iodine and molasses numbers. The last two factors give estimation as to the affinity of the coal towards low molecular number, and high molecular number organic effluents found in water. Both carbon reactors have been provided with automatic back-washing and air scouring facilities. These help extend the life of the reactor bed materials and their performance. This is performed automatically by the programmed logic system within the DCS of the refinery operations control room. Air is supplied through the refinery utilities plant air system which also provides aeration for the SBR. Water which is used for back-washing originates from the final storage pond, as that water is very clean and would be

Fig. 3.13: The quartz-type sand that is used to recharge the filters, the material is relatively fine and is granulated for effective absorbance of suspended particulates/pollutants.
sufficient to clean the filters. This reduces the need for the use of fresh water for environmental reasons. Figure 3.15 shows the carbon reactor vessels.

Fig. 3.14: The carbon that is used to recharge the filters, the material is relatively fine and has a high surface area for effective absorbance of dissolved pollutants.

Fig. 3.15: The two short white carbon filters on the LHS of the picture and the blue backwash drum overlooking the final storage pond.

3.3.10 Final Storage Pond

After the effluent water has passed through the carbon filters it is then stored in the final storage pond also known as the look-see basin (Fig. 3.16). This basin acts as the final checking point before the effluent is discharged to the harbour. The total capacity of the
look see basin is equivalent to about 540 m³ which is just over the discharge capacity of one SBR.

Fig. 3.16: The final storage pond, ("look-see" basin). Effluent standing before it is discharged using the valve which appears before the pond in the photograph.
CHAPTER FOUR
MATERIALS AND METHODS

4.1 INTRODUCTION

Water quality parameters must be determined accurately and such data are ascertained through appropriate sampling, storage and preservation, transport and testing techniques. This chapter considers the methods used to determine selected water quality parameters from the condensate refinery under study. Detailed description of the methods used for sampling, sample preservation, transport and testing techniques employed will be discussed. The exact location of the sampling points as well as the frequency of sampling are first presented below.

4.2 SAMPLING LOCATIONS AND FREQUENCY

Eleven locations within the treatment plant were sampled as shown in Fig. 4.1. Three of these locations (Location 1-3) are of the waste streams that have major contribution to phenol loading including desalter water, drain water, and neutralized spent caustic. Location 4 represents an average characteristic of all waste streams excluding the neutralized spent caustic (which is sent to a separate storage tank and then added directly under controlled conditions to some SBRs). This location is referred to as raw mixed inlet. The other 7 sampling points (4-11) are located at the outlets of the unit processes within the treatment plant. For example, sampling locations 5 and 6 are located at the outlet of the CPI separator and the outlet of the IGF unit, respectively.
Fig. 4.1 Process flow diagram extract for the Effluent Treatment Plant with sample locations (adapted from EPCL, 2002). Waste streams with + sign indicate intermittent flows. All indicated flow rates are obtained from the refinery operators directly and not design flows. Storage storm water is from tank bund walls, whereas pad storm water runoff is from open areas and roads.

The characteristics of the wastewater entering the different SBR are different. SBR-B receives treated waste streams leaving the IGF unit, while SBR-C receives a mixture of treated wastewater from the IGF unit, neutralized spent caustic and treated wastewater from the skimming pond. Two locations at the outlet of the SBR were thus chosen (Locations 7 and 8). The other sampling locations (Locations 9-11) include the outlet of the sand filter, the outlet of the activated carbon reactor, and the effluent pond.

To assess the effectiveness of the treatment plant, samples were collected from the sampling locations (see Fig. 4.1) on five different days during the period of December 30, 2003 to February 14, 2004 as shown in Table 4.1. Samples were further collected during 3-5 March, 05 for quantification of individual phenols in some waste streams and to assess fluctuation in waste characterization entering unit processes. Also, samples from other waste streams including boiler blow down, cooling water blow down, LPG vaporizer condensate, fuel oil heater condensate, caustic heater condensate, salt filter drain water, condenser drain water, diesel water
coalesor, kero water coalesor were tested on three separate occasions (19th - 21st of December 2005) for phenol concentration.

Table 4.1: Sampling dates and locations.

<table>
<thead>
<tr>
<th>Location</th>
<th>30/12/03</th>
<th>6-7/1/04</th>
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<th>8/2/04</th>
<th>14/2/04</th>
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<th>4/3/05</th>
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<td>X</td>
</tr>
</tbody>
</table>

* Analysis included quantification of individual phenols.
  b Samples where taken every 6 hours from 3-5/3/05.

4.3 WATER QUALITY PARAMETERS

Several water quality parameters have been chosen to be tested for in this study including: temperature, pH, total dissolved solids (TDS), dissolved oxygen (DO), oil and grease (O&G), COD, BOD5, TOC, sulphides, and phenols. Total phenols are determined by HACH method as well as UV spectrophotometric method and individual phenols are determined by gas chromatography with ECD detector as well as high performance liquid chromatography with fluorescence and photodiode array detectors.

This section defines the different water quality parameters in terms of what they represent and how they are analyzed. The section presents in some detail the testing procedure based on the APHA and US EPA test methods.

4.3.1 pH and Temperature

pH is the simple indirect measure of the hydrogen ion concentration in water and wastewater. The importance of pH in the water systems stems from the fact that many of the chemical reactions are dependant on pH. Many biological type reactions and systems function better at
certain pH ranges. The impact of increased risk of pollution from further reactions is also possible in high or low pH wastewaters in any system.

pH is determined following the Method APHA 4500 [APHA, 1998] given in [EPCL, Standard Water Analysis Manual, 2000] using a calibrated pH meter which also gives temperature of the sample being tested (Metrohm).

4.3.2 Total Dissolved Solids

Total Dissolved Solids in the wastewater basically include cations, anions and soluble organic compounds. TDS test is commonly used for testing polluted waters. The concentration of dissolved solids in water is, in fact, an important indicator of the usefulness of water for various applications. TDS (residue on evaporation) is the term applied to material left in a dish after evaporation of filtered water of a sample of water and subsequent drying in an oven at 110°C.

4.3.3 Dissolved Oxygen

DO is an important parameter for both industrial and domestic wastewaters that may be discharged into controlled waters such as rivers, stream and harbors as the impact of high oxygen demand in the waste may challenge the species available in the terrestrial water and will compete with them on the amount of DO available. This could consequently create serious problems. The importance of oxygen demand is detailed in the discussion on BOD determination. In-situ testing using combined meters is undertaken in the plant at the time of sampling. DO is determined by the APHA 4500 O-G Method [APHA 1998] given in [EPCL, Standard Water Analysis Manual, 2000]. Samples are analyzed using a DO meter (Orion) and expressed as mg/l.

4.3.4 Oil and Grease (O&G)

Oil and grease is an important indicator in both domestic and industrial wastewater quality determination, especially in refineries. A variety of organic substances including hydrocarbons,
oils and fats, waxes and high molecular long chain fatty acids and their esters with various fatty alcohols can be collectively referred to as oil and grease. Their importance in municipal and industrial wastes is related to their difficulty in handling and treatment. Because of low solubility, grease separates from water adhering to the interior of pipes and tank walls, reduces biological treat-ability of a wastewater, and produces greasy sludge solids which are difficult to process.

In this study, O&G was analyzed using "TOG/TPH analyzer" [EPCL, Standard Water Analysis Manual, 2000] (see Fig. 4.2) is also used for the determination of oil and grease in the samples. The sample is homogenized by vigorous mixing in the bottle the sample is received in and then placed on the specific glass window on a special slide and then analyzed by photometry using this meter which gives the reading as a direct measurement in mg/l.

Fig. 4.2: The O&G analyzer with the special slide that is inserted from the top [EPCL, 2003].

4.3.5 Chemical Oxygen Demand

COD is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. It is critical to note that the organic compounds and inorganic components (in reduced form) are subject to oxidation. However, in most cases the organic matter predominates. COD is widely used to characterize the organic strength of wastewaters and as a measure of pollutants in wastewater as well as natural waters. Other related analytical
values are BOD, and total oxygen demand (TOD). In most cases, it is possible to correlate these different parameters.

COD of the samples is analyzed following the standard test method APHA 5220 C [APHA 1998] given in [EPCL, Standards Water Analysis Manual, 2000] by digesting the sample with known volume of acidified potassium dichromate solution in a block digester (HACH) under controlled conditions and estimating the unconsumed dichromate with standard ferrous ammonium sulphate solution. COD values are expressed in units of mg/l as O₂.

4.3.6 Biochemical Oxygen Demand

BOD is the quantity of oxygen utilized by mixed population of micro-organisms in the aerobic oxidation at a specified temperature (20°C). The test measures, in particular, molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic matter (carbonaceous demand). Additional oxygen demand may be required at later times of incubation (more than 5 days) for the oxidation of nitrogen compounds by nitrite and nitrate bacteria (nitrogenous demand). Figure 4.3 illustrates the carbonaceous and nitrogenous oxygen demand as they might be exerted for a typical municipal waste. The BOD test is considered one of the most important tests of municipal or organic origin industrial wastewater. The widest application is probably the measurement of BOD for the determination of waste loadings on treatment plants and in the evaluation of the efficiency of the wastewater treatment system. The BOD test was performed following the standard test method APHA 5210 B [APHA 1998] given in [EPCL, Standards Water Analysis Manual, 2000] using the HACH BOD track monitor for an incubation period of 5 days thus referred to as BOD₅.
4.3.7 Total Organic Carbon

The TOC test measures the organically bound carbon in a water or wastewater sample. Unlike the COD, it is independent of the oxidization state of the organic matter. In this study, the TOC test was conducted following the standard test method APHA 5310 B [APHA 1998] given in [EPCL, Standards Water Analysis Manual, 2000] using a TOC analyser and the results are expressed as mg/l.

The device used for the determination of TOC is the TOC-1200 analyzer which operates on the principle of detection of carbon compounds in aqueous samples. The TOC-1200 provides the possibility to insert the sample in a module which can be introduced in the furnace. Once in the furnace, the sample becomes completely oxidized after which carbon dioxide (CO₂) that is formed can be measured with an NDIR detector giving total carbon (TC). When introducing the sample after the furnace, the inorganic compound (IC) may also be determined. TOC is therefore determined by subtracting the IC from the TC in the analyzed sample.
4.3.8 Phenols

Phenols are of great concern. They are very frequently found in refinery processes discharges and are the main focus of the present study. They are of particular concern as they come from a family of substituted aromatic compounds which are strongly associated with acute and chronic toxicity of marine life as discussed in Chapter Two. The formation of phenols in refinery processes is usually from desalter washings with the crude oil directly, tank water draws and from some of the other washing processes such as the caustic product washing (MEROX) units where conditions are favorable for their formation. In any case the determination of phenols is of great importance. Local Regulatory Agency (JAFZA/DM) in Dubai has a stringent regulation of 0.1 ppm for phenols in discharges into marine harbour waters. This in turn also means that the equipment and method being used for the determination of phenols must be accurate enough and have the appropriate tolerance to give this value.

Two methods are followed for the determination of phenols. A colorimetric method based on the reaction of phenols (unsubstituted, ortho and meta-substituted phenols) with 4-aminoantipyrine in the presence of potassium ferricyanide to form a coloured antipyrine dye (APHA 5530 C, 1998), given in [EPCL, Standard Water Analysis Manual, 2000] is used for the monitoring of phenols in the refinery. The HACH photometer (HACH Method 8047) was used in the study. Another spectrophotometer (Varian Series-Cary Win UV Spectra) was used to counter check the results obtained from HACH photometer as well as to analyze the samples containing high concentration of phenols such as neutralized caustic samples. Para substituted phenols (p-cresol, 2,4-dimethyl phenol, 2,4-dichlorophenol, 4-chloro-3-cresol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol, p-nitrophenol and pentachlorophenol) do not react in this method and cannot be estimated. The sensitivity of the method also varies with the type of phenols present in the sample. Because the water sample contains various phenols the results of the test are expressed as phenol (mg/l).
This necessitated the characterization of individual phenols in the sample. Individual phenols are determined by Gas Chromatography (US EPA 8041) as well as HPLC with fluorescence and photodiode array detectors (US EPA 555). In the GC method, a known quantity of the sample is extracted with dichloromethane, solvent is removed, and residue is dissolved in n-hexane and made up to a known volume. Target phenols in the extract are derivatized with pentafluorobenzylbromide (PFBBBr) and separated on a capillary column (CP-Sil 8, 30 m * 0.32 mm ID) and determined using electron capture detector. In the HPLC method, a known quantity of the sample is extracted with dichloromethane, solvent is removed, and residue is dissolved in acetonitrile and made up to a known volume. Phenols are separated using a gradient HPLC system with Symmetry ODS column (250 mm length x 4.6-mm id.) and determined using fluorescence and photodiode array detectors.

The characterization of phenols is carried out at the Central Laboratories Unit (CLU), UAE University. The individual phenols as well as total phenols in the samples are expressed as mg/l.

The following phenols were determined by the HPLC method:

- 2,4-Dinitrophenol
- 2-Methyl-4,6-dinitrophenol
- 2,4,6-Trichlorophenol
- 2,4-Dichlorophenol
- 2,4,5-Trichlorophenol
- Phenol
- m,p-Cresol
- o-Cresol + 2-cyclohexyl-4,6-dinitrophenol
- 2,3,4-Tetrachlorophenol
- 4-Chloro-3-cresol

The following phenols were determined using the Gas Chromatography Method with ECD:

- 2,4-Dimethylphenol
- o-Chlorophenol
- 2,6-Dichlorophenol
- o-Nitrophenol
- p-Nitrophenol
- Pentachlorophenol.
4.3.9 Summary of Test Methods

To summarize, the testing methods used in the laboratory for the determination of the above nine parameters are listed in Table 4.2.

Table 4.2 Method and instrument used to analyze for the target parameters.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference Method</th>
<th>Instrument Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>APHA 4500 HB</td>
<td>pH meter (Metrohm) (gives Temperature as well)</td>
</tr>
<tr>
<td>TDS</td>
<td>APHA 2540-C</td>
<td>Quantitative Analysis using HACH</td>
</tr>
<tr>
<td>DO</td>
<td>APHA 4500 OG</td>
<td>Cole Parmer</td>
</tr>
<tr>
<td>O&amp;G</td>
<td>APHA 5520 C</td>
<td>TOG/TPH Analyzer</td>
</tr>
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<td>APHA 5220 C</td>
<td>Behroitest</td>
</tr>
<tr>
<td>BOD</td>
<td>APHA 5210 B</td>
<td>HACH</td>
</tr>
<tr>
<td>TOC</td>
<td>APHA 5310 C</td>
<td>TOC-1200 Analyzer</td>
</tr>
<tr>
<td>Phenols</td>
<td>APHA 5530 D</td>
<td>Photometry (HACH)</td>
</tr>
<tr>
<td></td>
<td>US EPA 8041</td>
<td>Spectrophotometry (Varian Cary 50)</td>
</tr>
<tr>
<td></td>
<td>US EPA 555</td>
<td>Individual Phenols (Varian 3800 GC and Waters Alliance 2695 HPLC)</td>
</tr>
</tbody>
</table>

4.4 QUALITY CONTROL & QUALITY ASSURANCE

Appropriate QA/QC procedures are followed during sampling, transportation, storage and testing. An internal quality control system (blanks, replicates, spike and recovery etc) was followed to ensure the accuracy of the data obtained. The following conditions were observed:

4.4.1 Type of Container: When collecting samples for the eventual testing for a certain parameter, it is very important to select the appropriate container that will not in itself be the reason for false readings. These are such as placing phenol containing samples into a plastic type container which may absorb the phenol itself. Or in another example using a container which is see-through where a reaction between the parameter being tested for and the constituents would lead to a different concentration value from the time of sampling to the point of time that the sample reaches the laboratory because of the activation caused by UV-
sunlight intrusion into the bottle. Sample collection was carried out in this study using a glass type bottle with a high density polyethylene type bottle cap as shown in Fig. 4.4.

Fig. 4.4: Bottles are labeled and kept sealed until testing.

4.4.2 Preservation and Holding Time:

All samples were preserved and were tested before the elapse of the holding time specified by the APHA Method as indicated in Table 4.3.

Table 4.3: Summary of special sampling/handling requirements.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Container Type</th>
<th>Minimum Sample Size (ml)</th>
<th>Preservation</th>
<th>Holding time</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>Glass</td>
<td>100</td>
<td>Analyze immediately; add HCl to pH &lt; 2 and refrigerate</td>
<td>7 or 28 days</td>
</tr>
<tr>
<td>COD</td>
<td>Plastic or Glass</td>
<td>100</td>
<td>Analyze as soon as possible or add dilute H₂SO₄ to pH &lt; 2 and refrigerate</td>
<td>7 or 28 days</td>
</tr>
<tr>
<td>BOD₅</td>
<td>Plastic or Glass</td>
<td>1000</td>
<td>Refrigerate</td>
<td>6 to 48 hours</td>
</tr>
<tr>
<td>O&amp;G</td>
<td>Glass</td>
<td>1000</td>
<td>Add dilute H₂SO₄ to pH &lt; 2 and refrigerate</td>
<td>28 days in either case</td>
</tr>
<tr>
<td>Phenols</td>
<td>Glass</td>
<td>500</td>
<td>Add H₂SO₄ to pH &lt; 2 and Refrigerate</td>
<td>28 days under also further special conditions</td>
</tr>
<tr>
<td>TDS</td>
<td>Glass</td>
<td>500</td>
<td>Refrigerate</td>
<td>28 days</td>
</tr>
<tr>
<td>pH &amp; Temperature</td>
<td>Plastic or glass at normal ambient temperature</td>
<td>NA</td>
<td>Analyze immediately</td>
<td>NA</td>
</tr>
<tr>
<td>Turbidity</td>
<td>Plastic or Glass</td>
<td>NA</td>
<td>Analyze on the same day or store in dark up to 24 hours refrigerate</td>
<td>24 or 48 hours</td>
</tr>
</tbody>
</table>

Note that refrigerate at 4 ± 2°C, and plastic containers are high density type plastics to be used.

NA = Not applicable. Immediate analysis at EPCL means within one working shift = within 8 hours.

Adapted from APHA 1060 B [APHA, 1998]
4.4.3 Sampling

Sample bottles are washed and dried to ensure that they are clean for use. The sample bottles were rinsed with the sample several times prior to the sample collection in order to avoid any contamination arising from the sample bottles. Sample bottle is filled to the brim of the bottle to ensure that no reaction will occur with the air in the void space above the water level.

4.4.4 In-situ Testing

Any in-situ testing using portable probes is done on the same sample collected at the site at the time of sample collection. This is very important to be followed and the probes must be cleaned as to ensure that no cross contamination between samples is possible. In this study, temperature, pH, DO and TDS were determined at the sampling location except for the neutralized spent caustic and tank water drain draws samples which were tested within 15 to 20 minutes of being withdrawn from the sample point.

4.4.5 Transportation

Sealed and labeled sample bottles from the site are transported to the laboratory in the refinery vehicles within 10-15 minutes of sampling. In case, sampling time is longer, a cool box is used to store the samples during sampling and transportation. This was done with all the samples which were extracted from the refinery process plant to be tested in-house and also tested at the CLU at UAE University.

4.4.6 Safety

When dealing with wastewaters from domestic or industrial origin it is very important to ensure that the workers are kept safe from harm. Biological hazards, physical and chemical hazards
which exist in the samples and the reagents may cause serious illness and harm. Therefore, safety rules and regulations were strictly followed during sampling and sample analysis.

### 4.5 STATISTICAL ANALYSIS

Statistical analysis is required when the results are analysed to determine if functional relationships exist between the phenol level and the level of other parameters in the final effluent before discharge. This is in line with the main aim of this study, which is to ensure that the regulatory limits are adhered to by the EPCI refinery. The presence of a relationship may assist the operators in making a decision about adherence to discharge limits without the need to analyze for some parameters. Data collected for statistical analysis and data plots as shown in Chapter 5 have been chosen due to the consistent availability in the refinery over a period of five years, 2000-2004. It should be noted that data used represent daily final effluent pond readings for phenol, BOD₅, COD and sulphides. All data reported in which values were reported as “less than a certain value” where omitted from the scatter graphs plotted. Monthly averages were used in the correlation analysis as well.

The correlations were determined for phenol and other parameters including BOD₅, COD and sulphides. The significance of the relations was statistically verified using the method outlined by Anderson (1987). The 95% confidence limits (CI) of the slope were calculated using Eq. 4.1 and 4.2 [Anderson, 1987]:

\[
95\% \text{ CI} = \pm t_{a/2,n-2} \frac{s_{y,x}}{\sqrt{\sum x^2 - (\sum x)^2/n}}
\]  

(4.1)
Where, \( t \) is the student t value, \( \alpha \) is the level of significance, \( n \) is the number of data points, and \( s_{yx} \) is the standard deviation of \( y \) on \( x \) given by:

\[
s_{yx} = \sqrt{\frac{n-1}{n-2}(s_y^2 - b^2s_x^2)}
\]  \( (4.2) \)

Where, \( b \) is the slope of the best fit line for the data and \( s_y \) and \( s_x \) are the standard deviation of the \( y \) and \( x \) values, respectively.

Using the above equation, the 95% CI for the slope was determined for each relationship. The relationship is considered significant if the confidence interval of the slope does not pass through zero.
CHAPTER FIVE
RESULTS AND DISCUSSION

5.1 INTRODUCTION

With reference to the objectives stated in Chapter 1, this chapter compiles results from both the archive data which were available at the refinery and data which were collected during the course of this study. The discussion revolves around three main topic areas and they are:

a. A discussion and analysis of the most troublesome phenol-loaded wastewater streams is presented in Section 5.2. Also, under this section other chemical characteristics of the troublesome streams as analysed during this work are provided.

b. Section 5.3 discusses the performance of the ETP. In this section, phenol characterization at the different processes as well as the performance of the ETP in reducing phenol is discussed. The section concludes with a discussion on the behaviour of other wastewater quality parameters throughout the processes of the ETP.

c. Historical data collected from EPCL during 2000-2004 for the quality of treated wastewater are presented in section 5.4. The data include levels of phenol, COD, BOD$_3$ and sulphide in the final effluent pond of the ETP. The data are plotted to demonstrate the level of compliance with the stipulated regulatory standards. The data were further utilized to determine the nature of relationships, if exist, between phenol and other parameters (BOD$_3$/COD/ and sulphide). This has been carried out with the aim of determining the critical parameters in meeting the discharge limits set by the regulators. The relationship between BOD$_3$ and COD is also investigated in a similar manner in this section and conclude the chapter.
5.2 TROUBLESOME WASTEWATER STREAMS

5.2.1 Identification of Troublesome Wastewater Streams

In the analysis of the basic problems and challenges in meeting the regulatory specifications from the JAFZA, through the discussions with EPCL refinery employees and their confirmation on the most troublesome wastewater streams in addition to the review of the design data based on Table 3.1, the following three streams are considered the most troublesome; desalter effluent, neutralized spent caustic, and tank water drains. The design phenol levels of these streams are: 10, 10 and 238 mg/l, respectively. It is to be further noted that although for the tank water drain and desalter effluent the design is only 10 mg/l, refinery employees have confirmed, through refinery laboratory analysis, much higher levels recorded in both streams depending on the type of crude in the tanks that is being dewatered or being sent for oil processing.
5.2.2 Sample Description

This section describes the samples collected from the troublesome waste streams. Physical parameters such as colour, appearance, odour in addition to a typical photograph of the sample of that wastewater stream are recorded.

5.2.2.1 Neutralized spent caustic

Location: Sampling point 3 Fig. 4.1 (Tank 22D-109)

Colour: Dark greenish-yellow liquid.
Appearance: Liquid with black floating and settleable particulate matter (Fig. 5.1). Some black/brown residues were also floating on the top surface of the sample.
Odour: A blend of very strong, pungent petroleum and sulphide type odour.

![Neutralized spent caustic sample](image)

Fig. 5.1: Neutralized spent caustic sample

5.2.2.2 Desalter wastewater

Location: Sampling point 1 Fig. 4.1.

Colour: Colourless liquid (white with cloudiness)
Appearance: Heavy suspension brackish water with brownish residual light particles in suspension, the liquid is also very cloudy (Fig. 5.2).
Odour: A relatively pungent mixture of saltish petroleum odour.
5.2.2.3 Tank draw wastewater

Location: Sampling point 2 Fig. 4.1. Drain water from 23D-102, crude condensate storage tank.

Colour: Dark yellow to brownish in colour (due to the highly oxidized iron content).

Appearance: Liquid with black floating and settleable sediments, in addition to some dark particle/residues also floating on the top surface of the sample (Fig. 5.3).

Odour: A blend of very strong, pungent petroleum and sulphide type odour.
5.2.3 Troublesome Wastewater Stream Characteristics

The wastewater streams were tested for several parameters during the study period and the values (range and average) are presented in Table 5.1. The table gives an indication of the characteristics of the wastewater streams identified as troublesome. Discussion and summary of the results presented in Table 5.1 is given in the subsections below.

Table 5.1: Characteristics of the three main troublesome waste streams.

<table>
<thead>
<tr>
<th>Wastewater stream</th>
<th>Typical Flow rate</th>
<th>pH</th>
<th>TDS (mg/l)</th>
<th>COD (mg/l)</th>
<th>Phenols (mg/l)</th>
<th>O&amp;G (mg/l)</th>
<th>DO (mg/l)</th>
<th>TOC (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Desalter effluent (Continuous)</td>
<td>Average: 7 m³/hr/unit</td>
<td>7.5</td>
<td>129</td>
<td>753.5</td>
<td>0.95</td>
<td>&lt;5</td>
<td>3.7</td>
<td>118</td>
</tr>
<tr>
<td></td>
<td>Max: 7.9 m³/hr/unit</td>
<td>7.8</td>
<td>310</td>
<td>916</td>
<td>1.33</td>
<td>&lt;5</td>
<td>5.5</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>Min: 6 m³/hr/unit</td>
<td>6.5</td>
<td>20</td>
<td>552</td>
<td>0.25</td>
<td>&lt;5</td>
<td>1.8</td>
<td>114</td>
</tr>
<tr>
<td>Neutralized spent caustic (Batch)</td>
<td>Average: 80 m³/week</td>
<td>7.0</td>
<td>2432</td>
<td>11093</td>
<td>180.0</td>
<td>87</td>
<td>2.07</td>
<td>5212</td>
</tr>
<tr>
<td></td>
<td>Max: 160 m³/week</td>
<td>7.1</td>
<td>65230</td>
<td>17100</td>
<td>306</td>
<td>110</td>
<td>3.2</td>
<td>5212</td>
</tr>
<tr>
<td></td>
<td>Min: 80 m³/week</td>
<td>6.8</td>
<td>11560</td>
<td>5220</td>
<td>112</td>
<td>56</td>
<td>1.1</td>
<td>5212</td>
</tr>
<tr>
<td>Water drain from condensate tanks (Intermittent/Batch)</td>
<td>Average: 20.4 m³/batch</td>
<td>5.87</td>
<td>27385</td>
<td>34608</td>
<td>65.34</td>
<td>126</td>
<td>1.3</td>
<td>22215</td>
</tr>
<tr>
<td></td>
<td>Max: 263 m³/batch</td>
<td>6.1</td>
<td>86570</td>
<td>108100</td>
<td>330.0</td>
<td>217</td>
<td>2.5</td>
<td>39180</td>
</tr>
<tr>
<td></td>
<td>Min: 0 m³/batch</td>
<td>5.6</td>
<td>14562</td>
<td>5250</td>
<td>0.63</td>
<td>8</td>
<td>0.3</td>
<td>5250</td>
</tr>
</tbody>
</table>

1 Tabulated results are based on analysis of 6 samples collected from each of the desalter effluent and water drain and 7 samples collected from the neutralized spent caustic waste stream.
2 Based on information obtained through verbal discussions with refinery operators.
3 Phenol values are based on the EPCL (HACH Method) analysis.
4 The flow from the neutralised spent caustic drum is sent into a storage tank at the ETP where the contaminated effluent is fed into the sequencing batch reactors (C and D) mixed with ETP processed effluents at a ratio range of 25-35% (SBR influent: neutralized spent caustic).
5 Batches are considered after each importation of crude condensate

5.2.3.1 Neutralized Spent Caustic

The dark colour observed in this sample is due to the presence of sulphides. The neutralized spent caustic is a mixture of many different compounds generated in the MEROX processes. The dark colour of the sample is due to the presence of sulphides. The strong sulphide odour indicates the presence of sulphides. As shown in Table 5.1 and by comparison to Table 3.1 we find that the pH
range for this sample falls in the design range. The design parameter values for COD, TDS, O&G and phenols are much higher than the actual values found in the analysis of samples during this study. An average of 80 m$^3$ of neutralised spent caustic is generated per week and at times of very high production the waste stream doubles to 160 m$^3$ per week. All the spent caustic goes to a holding storage tank where it is stored and slowly processed through the ETP.

5.2.3.2 Desalter Effluent Water

The desalter effluent water shows consistency in pH range with the design values for this stream. The TDS is significantly lower by 10-fold in reality when compared to the design value. The COD for this stream is around 800 mg/l as expected. However, it should be noticed that the average COD value is less than the design value but the maximum value recorded exceeded the average design value by 66 mg/l. The actual phenols obtained during the analysis (average 0.95 mg/l) are much lower than the 10 mg/l design value. The O&G level in the desalter effluent (< 5 mg/l) is also significantly less than the 200 mg/l estimated design value. The desalter generates an average outflow rate equal to 7 m$^3$/hr/unit with two desalter units in the whole refinery.

5.2.3.3 Tank Drain Water

The tank drain water was generally discoloured due to the presence of iron in the sample. Petroleum odour is expected as the drain water has leached from the condensate. The average pH value is lower than the design value. The recorded average value was 5.87 as compared to the design range of 7 to 9 (refer to Appendix 1, stream 13 on P&ID). The actual TDS value is 10-fold higher than the expected design value. However, the COD values recorded (average 34,608 mg/l) are much higher than the design value of 850 mg/l. This was also, to a much lesser extent, the case with the phenol where the determined average value was 65.34 mg/l as opposed to 10 mg/l. But the wide range of phenol values shows that this stream is extremely varied depending on the condensate crude that was in the tank the water was drawn from. However, determined oil and grease values are about 10-fold less than the design value of 10,000 mg/l. The tank water drain wastestream is generated from the removal of wastewater from the crude condensate tanks. This is usually done after receipt of the crude into the
storage tanks. The tanks water drain wastewater is therefore a batch process in which batches can range from 0 to 260 m$^3$ of wastewater. The average wastewater volume drawn from any tank for any batch is around 20 m$^3$. All the wastewater goes to the ETP diversion box in an intermittent manner and any high flows are diverted to the surge pond where the wastewater mixes with the other plant influent stored in the surge pond.

5.2.3.4 Other Wastewater Streams Going to the ETP

There are other wastewater streams that flow into the ETP from the plant are contaminated waste streams. These can be reviewed from the process and instrumentation diagram in Appendix 1. To summarize, below is a description of each stream and the typical range of values of phenols and flow rates as per the operational data collected from the control and field operators in the refinery.

a. Sour water stripper (SWS) wastewater is a product of any units that may potentially contain hydrogen sulphide (H$_2$S) and ammonia in the plant. This may arise, for example, from the plant overhead drums, acid gas knock out drums, etc. The SWS wastewater is sent to the desalter where it is used as wash water. Typical flow rate into the desalter through the wash water drum ranges between 0.4-6 m$^3$/hr per condensate distillation unit (CDU) of which two exist in the plant. The stripped sour water is stored in the wash water drum and the difference of wash water is made up through topping up the storage wash water drum with plant utility water. Thus, no data are available for the SWS wastewater stream independently as the refinery operatives test the desalter water outlet (brine water) after mixing and process only. Stripped sour wastewater is produced on an intermittent basis depending on the oil processing activities.

b. Boiler blowdown water is produced from the boiler activities. The blowdown rate ranges from 0.4 to 1 m$^3$/hr per CDU and the flows are continuous. The phenol concentrations in these streams (tested on three separate days) were lower than 0.003 mg/l. The phenol contribution from boiler blowdown is insignificant to the ETP influent.
c. Cooling water blowdown is produced from the refinery cooling tower operations. The blowdown rate ranges from 3 to 5 m³/hr for 22 hrs in every 24 hrs. The blowdown is ceased for 2 hrs at which time the refinery operatives dose the cooling tower with a chemical for biocide control. Once a month, the tower is shutdown for a whole day of maintenance and inspection. The phenol concentrations in these streams (tested on three separate days) were lower than 0.003 mg/l. Thus, phenol contribution from the cooling water blowdown is insignificant to the ETP influent.

d. Condensate wastewater generated from the LPG vaporizer, fuel oil line heater and caustic heaters range at 0.2–0.5 m³/hr, 0.5–1 m³/hr and 0.5–1 m³/hr, respectively. There is one LPG vaporizer and one fuel oil heater but the flow rates may double depending on the CDU operational processing rates. Therefore, the above rates can double when both distillation columns are running in full swing. Wastewater production flows from the caustic heater and fuel oil heater are continuous whereas that of the LPG vaporizer is intermittent. The phenol levels in all three streams were tested on three different days and all the results showed phenol concentrations less than 0.003 mg/l. Again, the phenol contribution from the condensate wastewater is insignificant to the ETP influent.

e. Oily water from the salt filters is removed in every shift through a drain valve and thus produced on an intermittent basis. The removed oil water is drained at a rate of typically 10-15 litres in every shift (i.e. every 8 hrs) where the drain will be opened for less than 5 minutes. The phenol levels recorded for this stream (on three separate days) were 54, 56.7 and 78 mg/l. Although the phenol concentration is relatively high in this stream the flow rate is small. Thus, this stream does not contribute significantly to phenol loading on the ETP.

f. Oily water from the Kero water coalescer is drained on a continuous basis at a rate of 0.5–1 m³/hr per unit of which there are two, each one serving one CDU. The phenol levels (tested on three separate days) were found to be 0.10, 0.22, and 0.28 mg/l. The values and flow rates from these units is small. Thus, phenol contribution from this stream to loading of the ETP influents is considered insignificant.

g. Oily water from the Diesel water coalescer is drained on a continuous basis at a rate of 0.5–1 m³/hr per unit of which there are two, each one serving one CDU. The phenol levels of this stream
(tested on three separate days) were found to be 0.18, 0.05, 0.22 mg/l. The values and flow rates from these units are small, again leading to an insignificant contribution to phenol loading.

h. As far as tank farm storm water and surface run off from rain is concerned during the period of this study, it was not possible neither to collect samples and analyse for phenol nor calculate typical flow rates. However, it is unlikely, that phenol contamination exists in rain water.
5.2.3.5 Phenol loading from waste streams

For evaluation purposes, all of the wastewater streams are discussed below and the results of a comparative phenol loading from all wastewater streams are presented.

Neutralized spent caustic is produced on intermittent basis at a rate of 80-160 m$^3$/week. The wastewater stream is stored in a dedicated tank in the ETP and is fed under controlled conditions into the ETP processing units directly in-line mixing whilst mixing with plant SBR influent. The average phenol concentration recorded from testing during this study was about 180 mg/l although the maximum recorded value has been over 306 mg/l. The average phenol loading is equivalent to 1497.6 kg/yr.

There are two desalters in the refinery. The desalter generates an average outflow rate of 7 m$^3$/hr/unit. The deslater inflow wash water is made up of SWS wastewater as well as plant utility make-up water. Phenols concentrations obtained during the analysis (average around 0.95 mg/l) are much lower than the 10 mg/l design value. The maximum phenol concentration recorded was 1.3 mg/l. The phenol loading on the ETP from both units is equivalent to an average of 131.6 kg/yr.

Tank water draws are produced on an intermittent basis. The wastewater produced from the tank drains varies greatly from nil to 262.7 m$^3$/batch. The phenol concentrations also vary from 0.63-300 mg/l. Any excess tank drain wastewater received by the plant is diverted to the ETP surge pond for short term storage before processing through the ETP units. With an average phenol concentration of 65.34 mg/l and an average flow of 20.4 m$^3$/batch, the average phenol loading on the plant is equivalent to 1.33 kg/batch with a maximum of two batches (i.e. two import shipments) per week. However, it is interesting to note that based on a receipt of maximum 262.7 m$^3$, the loading of phenol would increase to 17.16 kg/batch which is very significant. Based on the annual data collected from the shipping records in the year 2004 of crude condensate received in the refinery which includes the average water content per parcel delivered, the phenol loading would average 69.3 kg/yr.
Other wastewater streams originating from the boiler and cooling water blow down, polluted heater and vaporizer condensates, Merox plant oily water from the salt filters, oily water Kero and diesel coalescers as well as rain water do not contribute any significant phenol loading on the ETP influent. Table 5.2 summarizes the characteristics of all the wastewater streams with their corresponding flow rates, average phenol concentration and annual phenol loadings.

Table 5.2: Phenol loading on the ETP

<table>
<thead>
<tr>
<th>Waste stream</th>
<th>Flow rate</th>
<th>PHENOL</th>
<th>Phenol loading(^1) kg/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td><strong>Average mg/l</strong></td>
<td><strong>Std Deviation</strong></td>
</tr>
<tr>
<td>Neutralised spent caustic</td>
<td>80-160 m(^3)/week</td>
<td>180.03</td>
<td>69.53</td>
</tr>
<tr>
<td>Desalter wastewater</td>
<td>6-7.9 m(^3)/hr/unit</td>
<td>0.95</td>
<td>0.5</td>
</tr>
<tr>
<td>Tank drain draw wastewater(^2)</td>
<td>0-262.7 m(^3)/batch</td>
<td>65.34</td>
<td>130.06</td>
</tr>
<tr>
<td>Sour water wastewater</td>
<td>0.4-6 m(^3)/hr</td>
<td>All flows go through the desalter</td>
<td>All flows go through the desalter</td>
</tr>
<tr>
<td>Boiler blowdown wastewater</td>
<td>0.4-1 m(^3)/hr</td>
<td>&lt;0.003</td>
<td>NA</td>
</tr>
<tr>
<td>Cooling water blowdown wastewater</td>
<td>3.5 m(^3)/hr</td>
<td>&lt;0.003</td>
<td>NA</td>
</tr>
<tr>
<td>Condensate LPG wastewater</td>
<td>0.2-0.5 m(^3)/hr</td>
<td>&lt;0.003</td>
<td>NA</td>
</tr>
<tr>
<td>Condensate fuel heater wastewater</td>
<td>0.5-1 m(^3)/hr</td>
<td>&lt;0.003</td>
<td>NA</td>
</tr>
<tr>
<td>Condensate caustic heater wastewater</td>
<td>0.5-1 m(^3)/hr</td>
<td>&lt;0.003</td>
<td>NA</td>
</tr>
<tr>
<td>Salt filter wastewater</td>
<td>0.00156 m(^3)/hr</td>
<td>62.9</td>
<td>13.15</td>
</tr>
<tr>
<td>Kero water coalescer wastewater</td>
<td>0.5-1 m(^3)/hr</td>
<td>0.2</td>
<td>0.092</td>
</tr>
<tr>
<td>Diesel water coalescer wastewater</td>
<td>0.5-1 m(^3)/hr</td>
<td>0.15</td>
<td>0.089</td>
</tr>
<tr>
<td>Storm water(^3) from tank farm and pad run-off</td>
<td>NA</td>
<td>Not tested</td>
<td>NA</td>
</tr>
</tbody>
</table>

\(^1\) Annual phenol loading has been calculated using the maximum hourly/weekly flow rates (production) and the average phenol concentration in the waste stream.

\(^2\) The total quantity of tank drain water was obtained from the shipping records of the refinery for 2005 with a total received tank drain water of 1060.8 m\(^3\). It is not possible to calculate an hourly rate due to the intermittent flow nature of the stream in addition to the fact that quantities received in one shipment fluctuate from 0 to 200 m\(^3\) of wastewater.

\(^3\) Storm water from the tank farms originates from storm water contained inside the tank bund area, whereas pad run-off is attributed to storm water originating from open concreted areas within the process plant and roads.
5.2.4 Characterization of Phenols in the Troublesome Wastewater Streams

Three fingerprint plots for phenols have been made for the main troublesome streams using the phenols data collected for the tank drain water, neutralized spent caustic and the desalter water. These are shown in Figs. 5.4-5.6. Discussion of these results is presented below.

5.2.4.1 Tank drain water phenols characterization

Figure 5.4 shows the concentration of 16 different phenols and total phenol in the tank drain wastewater stream. The figure shows results of samples collected from two separate tanks, tank 23D-103 and tank 23D-101, both containing different crude condensates. The concentration of phenols varies significantly with certain types of phenols such as cresols, 2,4-dimethylphenol and 2,6-dichlorophenols. The non-existence of 5 to 7 out of 15 compounds is evident in both samples indicating that cresols, 2,4-dimethylphenol and 4-chloro-3-cresol as well as o-cresol + 2-cyclohexyl-4,6-dinitrophenol compounds are probably consistently available in the condensate tank waste steam. Furthermore, m, p-cresols seems to be the highest in concentration recorded after phenol and shows similar peak concentrations as o-cresol + 2-cyclohexyl-4,6-dinitrophenol. These compounds are probably found due to chemicals added during exploration and pretreatments which are undertaken on the crude condensate prior to arrival at the refinery as indicated in Chapter 2. Other nitro and chloro-phenol are present in small amounts.
5.2.4.2 Neutralized spent caustic wastewater phenols characterization

Figure 5.5 shows the concentrations of the 16 different phenols and total phenol in the neutralized spent caustic waste stream. Most of the phenol compounds present in this waste stream are similar to those found in the tank draw waste stream. These include 2,4,6-trichlorophenol, m,p-cresols, 2,3,4-tetrachlorophenol, o-cresol + 2-cyclohexyl-4,6-dinitrophenol and phenol. However, in this waste stream, o-cresol + 2-cyclohexyl-4,6-dinitrophenol and m,p-cresols are detected in concentrations nearly equal to that of phenol. The non-existence of 10 out of 15 compounds is evident. The 5 phenol compounds detected in this waste stream are probably products of the Merox and subsequent neutralization reactions that take place in the plant operations. These are found due to possibly the violent catalysis oxidation reactions and subsequent acid-base reactions (neutralization) that take place in the reactors on the final raw products prior to final product
storage and export from the refinery. Again, phenol and m-cresol seem to be the highest in concentration among other phenols.

Fig. 5.5: Characterization “fingerprint” plot of phenols for neutralized spent caustic.

5.2.4.3 Desalter effluent wastewater phenols characterization

Figure 5.6 shows the concentrations of the 16 different phenols and total phenol in the desalter waste stream on the 2 sampled days. The variations of phenols are very much consistent. Again we find that straight phenols and cresols are highest in the stream at nearly equal levels. Also, 2,4,6-trichlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, o-cresol + 2-cyclohexyl-4,6-dinitrophenol, 2,3,4-trichlorophenol, and 2,4-dimethylphenol, exist in nearly equal concentrations in both samples tested. Furthermore, 4-chloro-3-cresol and 2,6-dichlorophenol are present in this wastewater stream as well.
Based on the two sampling routines, it is evident that the levels of phenol derivatives are less than the levels in the drain water and the neutralized caustic streams. The desalter sample is very much dependent on the contents of the condensate which it washes. The maximum availability of phenols as a total does not exceed the range of 0.5-0.6 mg/l which is less than that of the tank wastewater stream (1.0-3.5 mg/l) and much less than the levels in the neutralized spent caustic which lie between 30 and 110 mg/l. The low level of phenols in this waste stream is most probably due to the low solubility and dissociation of phenol compounds as discussed in Chapter 2.

From the characterization phenols in the troublesome streams it is evident that:

1. The ratios of the same phenol compounds is quite similar in most cases, but it is noted that the tank drain waste stream show greatest variations based on the different crude condensate tanks that drain water originates from.

2. Phenol and m,p-cresols are the most dominant phenols in the waste streams.
3. Phenol, m,p-cresols, o-cresol, tri and tetra-chlorophenols and to a lesser extent 4-chloro-3-cresol are common among these streams.

It should be noted that the formation of substituted phenols in the aforementioned waste streams may depend upon several factors including: the structure of the molecule, favourable position in the benzene ring for substitution, favourable temperature for the formation of that particular compound, the pH of the stream, and competition of other compounds such as chlorine and nitrogen containing compounds in the stream.
5.3 PERFORMANCE OF THE EFFLUENT TREATMENT PLANT (ETP)

5.3.1 Sample Description

With reference to the samples that were tested through the process, below is a description of typical samples tested from the different treatment processes in the ETP. Parameters included in sample description are colour, appearance, and odour.

5.3.1.1 Diversion box (CPI- Inlet) water

Location: Sampling point 4 Fig. 4.1.

Colour: Yellowish liquid (slightly cloudy)

Appearance: Liquid with floating and settleable sediments, with heavy suspension of black particles (Fig. 5.7).

Odour: A petroleum oily type smell which is relatively pungent.

![Diversion Box (CPI-Inlet) wastewater sample](image)

5.3.1.2 CPI outlet/IGF inlet

Location: Sampling point 5 Fig. 4.1.

Colour: Greenish-yellow tinted liquid (slightly cloudy)

Appearance: Liquid with floatable and settleable particulate matter. Heavy suspension in the liquid with some black particles (Fig. 5.8).

Odour: A petroleum oily type smell which is relatively pungent.
5.3.1.3 IGF outlet/SBR inlet

**Location:** Sampling point 6 Fig. 4.1.

**Colour:** Greenish-yellow tinted liquid (slightly cloudy)

**Appearance:** Liquid with floatable and settleable particulate matter. Heavy suspension in the liquid with some black particles (Fig. 5.9).

**Odour:** A petroleum oily type smell which is slightly pungent.

5.3.1.4 SBR B Outlet/Inlet to the settling pond/sand filter inlet

**Location:** Sampling point 7 Fig. 4.1.

**Colour:** Clear slightly greenish tint liquid.

**Appearance:** Liquid with small brownish settleable particulates (Fig. 5.10).

**Odour:** A slight petroleum oily type smell.
5.3.1.5 Sand filter outlet/Carbon bed inlet

Location: Sampling point 9 Fig. 4.1.

Colour: Relatively opaque and clear liquid and colourless.

Appearance: Liquid with some settleable particulates with a very slight suspension but making the sample relatively opaque but also with slight cloudiness (Fig. 5.11).

Odour: A very slight petroleum oily type smell.

5.3.1.6 Carbon bed outlet

Location: Sampling point 10 Fig. 4.1.

Colour: Opaque, colourless and clear liquid.

Appearance: No significant suspension or settleable particulates can be seen (Fig. 5.12).

Odour: No detectable smell.
5.3.1.7 Final effluent pond (Look-See Basin)

Location: Sampling point 11 Fig. 4.1.

Colour: Opaque, colourless and clear liquid.

Appearance: No significant suspension or settleable particles can be seen. A few slight particles settled at the bottom of sample bottle, probably from algal growth in the final discharge pond (Fig. 5.13).

Odour: no detectable smell.
5.3.2 Effluent Parameter Through the Treatment

Samples were collected and analysed from the inlet and outlet of the ETP units to investigate temporal variation of parameter values. Samples were collected at every six hour intervals over a period of 48 hrs. Figures 5.14-5.18 show the results (of the tested parameters) and indicate the general trends during monitoring. The results are further discussed below.

5.3.2.1 pH

Figure 5.14 shows variations in the pH value of the inlet and outlet of the ETP units. Typically, the pH stays within a range of 6.5 to 7.5. This is expected because there are no additives that would change the pH drastically. As the SBR is a batch process that results in homogenization of the incoming streams, we find that the pH values of the inlet sand filter and inlet carbon bed are relatively steady at around 7.2. It should be noted that the pH is an important parameter to be controlled during treatment of the effluent in the SBR.

![Fig. 5.14: pH variation with time over 48-hr duration](image.png)
5.3.2.2 Temperature

Figure 5.15 shows variations of temperature of incoming and treated effluent for each unit process. Sampling started at midnight which is typically a cooler time of the day. The ambient temperature play a major part in affecting the effluent temperatures throughout the processes, the peak temperatures are typically at midday with the cycle lowest temperature at midnight and highest at midafternoon. The temperature does not differ much between different processes and the trend is alike for all processes.

![Temperature variation with time over 48-hr duration](image)

5.3.2.3 TDS

Variations in the TDS of the incoming and treated effluent for each unit process are demonstrated in Fig. 5.16. TDS variations in the CPI and IGF seem to be very much related to variation in the TDS of the inlet to the treatment plant. It is not evident that the initial CPI and IGF processes have any real impact on TDS where there is no change between inlet CPI TDS values and those of the outlets of the CPI and the IGF. The TDS for the outlet of the SBR, sand filter and carbon bed does not fluctuate much but is at higher value than that of the CPI and IGF. Little fluctuation in the TDS of the inlet sand filter and carbon bed is due to homogenization of waste streams in the SBR. Higher TDS at the inlet of these units is probably due to that fact that the SBR increases the
TDS levels due to the dosing of nitrogen compounds and phosphates through addition of urea and phosphoric acid to assist in SBR action.

5.3.2.4 COD

Variations in the COD of the incoming and treated effluent for each unit process are shown in Fig. 5.17. Although there are significant variations in the COD of the influent of the CPI, IGF and SBR, there is not a particular trend of increase or decrease of the parameter value within the monitoring duration. The influent IGF has generally higher COD than that of the stream entering the CPI. This is possibly due to dissolution (emulsification) of some of the organic matter in the CPI that was originally not dissolved when the stream entered the CPI itself. It is also noted that the COD level entering the SBR is almost similar to that entering the IGF, indicating that the IGF does not remove COD.

However, the graph reveals that the SBR process is very effective in removing COD as demonstrated by the significant drop in the COD of the inlet to the sand filter compared to the levels at the outlet of the IGF. The graph also demonstrates that the sand filter has practically no effect on COD reduction as the values at the inlet of the sand filter and the inlet of the carbon bed remain the same.
It is interesting to note the high fluctuations of COD in the ETP influent. A possible explanation of this is the intermittent flow from the tank water that is usually high in COD (refer to Table 5.1) as compared to other continuously flowing wastewater streams such as the desalter and blow-down waste streams.

![COD Variation with Time](image)

Fig. 5.17: COD variation with time over a 48-hr duration

5.3.2.5 Phenol

Figure 5.18 shows variations of phenols in the incoming and treated effluent of each unit process (tested using HACH and UV methods). The values of phenol in treated wastewater preceding the SBR fluctuate between 0.5-1.5 mg/l. After the SBR treatment, phenol levels drop to around 0.1 mg/l.

Figure 5.18 further shows a similar trend of phenol fluctuations as that of the COD. Again, the SBR has the most effective impact on the reduction of phenols due to degradation of phenol in the reactor.
5.3.3 Reduction of Phenol across ETP Process Units

Total phenol removal across the ETP processes is illustrated in Fig. 5.19. The figure clearly depicts the effect of the SBR on phenol reduction. The physical and chemical separation units (CPI and IGF) do not have any real effect on phenol removal as similar phenol levels (compared to the entering waste stream) are observed in the outlet of these processes. The observed slight increase in phenol in the sand filter and carbon bed could be due either to experimental errors or time lag.
in collecting the samples. The carbon reactor has a positive effect on removal of phenol as depicted by the decrease in the level of phenol in the effluent pond as compared to the inlet of the carbon bed. Figure 5.19 also illustrates the fluctuation in the phenol level entering the ETP which ranges between 0.3-1.5 mg/l. This range could even be wider if samples were taken over longer durations. Such fluctuations are mainly attributed to varying phenol levels in the desalter and tank drain wastewater streams.

![Figure 5.19: Change in Phenols across process units in the ETP taken at different times. Symbols represent different data sets taken on different days](image)

5.3.4 Behaviour of Wastewater Parameters Across the ETP Units

Analysis results for samples collected in this study from the ETP units are utilized to generate graphs that describe the behaviour of the different parameters tested across the unit processes. The processes described in this section include the CPI, IGF, SBR, sand filter and carbon bed. Samples were collected across (influent and effluent) each process.
5.3.4.1 Changes in Temperature

Figure 5.20 shows that the temperature variation is quite insignificant, fluctuating by about one degree in any day and no more than nine degrees between different sets of data due to time of day of sample extraction. Thus, temperature values mainly depend on the time of the day the samples were drawn.

Fig. 5.20: Change in temperature across process units in the ETP taken at different times.

Symbols represent different data sets taken on different days

5.3.4.2 Changes in pH

Figure 5.21 shows that the variations in pH are not high with a maximum change of about one unit throughout the whole plant. This is probably because the mixed inlet comes from many different streams and thus shows a particular characteristic mixture pH. The pH is generally controlled as the SBR selective bacteria require stable pH values. Although not clearly demonstrated in the graph, the pH is expected to drop slightly in the SBR due to the addition of phosphoric acid that is needed as a source of phosphorus for the bacteria.
Fig. 5.21: Changes in pH across process units in the ETP taken at different times.
Symbols represent different data sets taken on different days

5.3.4.3 Changes in TDS

Figure 5.22 shows that for the same sampling period the TDS remains almost the same in the CPI and IGF but changes as the waste received changes for different periods. The wastewater in the SBR usually has higher TDS than the level in previous unit processes due to the high level of TDS in the received neutralized spent caustic (Table 5.1) that is not processed in the CPI or IGF. The inlet and outlet of the sand filter retains almost the same TDS value for a certain processed batch. Also as discussed above, higher TDS at the inlet of these units could be due to that fact that the SBR increases the TDS levels due to the dosing of nitrogen compounds and phosphates through addition of urea and phosphoric acid to assist in SBR action.
Fig. 5.22: Changes in TDS across process units in the ETP taken at different times. Symbols represent different data sets taken on different days.

5.3.4.4 Changes in dissolved oxygen (DO)

Fig. 5.23 shows that the DO content in the influent of the ETP is generally low. This is probably due to the consumption of oxygen that takes place in the diversion box due to the high organic loadings of the waste. The DO increases significantly with the air injection that takes place in the SBR. The oxygen remains constant afterwards throughout the polishing processes giving an indication that there are no significant biodegradable organic pollutants to consume the oxygen in the later stages. The DO increases in the final effluent pond as it is ejected from a height onto the surface of the pond causing aeration of the effluent.
Fig. 5.23: Changes in DO across process units in the ETP taken at different times. Symbols represent different data sets taken on different days

5.3.4.5 Changes in chemical oxygen demand

Figure 5.24 shows that the COD is reduced significantly through the SBR process, with the concentration dropping from an average of 472-510 mg/l across the CPI and IGF to 125 mg/l after the SBR. The SBR is the most effective process in reducing the COD. It is possible that degradation still takes place across the sand filter causing such reduction while sorption as well as some degradation might be active in the carbon bed.
5.4 RELATIONSHIP BETWEEN PHENOL AND OTHER WATER QUALITY PARAMETERS

In this section, historical data collected from EPCL during the years 2000-2004 for the quality of treated wastewater in the final effluent pond are utilized to analyse regulatory compliance trends and to determine the nature of relationships, if exist, between phenol and other parameters (BOD$_3$/COD/ and sulphide). This is with the aim of determining the critical parameters in meeting the discharge limits set by regulators. The relationship between BOD$_3$ and COD is also investigated in a similar manner.

5.4.1 Analysis of Historical Data and Regulatory Compliance of Final Effluent

In investigating the level of compliance of the final processed effluent with the stipulated regulatory standards, the data for the five years (2000-2004) were plotted for every day on a plot of concentration versus time. This was done for the four parameters: phenol, BOD$_3$, COD and
sulphides (see Fig. 5.25). A straight line also appears on each plot and represents the regulated monthly average limit of that parameter.

It should be emphasized here that the ETP was commissioned in 2000. Meanwhile, discussion with the EPCL refinery operatives revealed that in 2004 the condensate distillation columns (main oil processing units) were shut down for some time interchangeably throughout the year. Due to the reduced wastewater stream that flows from the daily operations, entering the ETP during 2004, the refinery operatives attempted to maximize processing of stored wastewaters from the surge pond and also by processing greater amounts of stored neutralized spent caustic through the four operating SBR units.

As obvious from Fig. 5.25, the concentration of phenol, COD, BOD₃ and sulphide in the final effluent exceeded the regulations for the major part of the first one and half years of operation where the final effluent in many cases was reprocessed or diluted before discharge. The monthly averages for the period were also high with reference to the records. However, from August 2001 onwards, the daily readings of these parameters started complying to a much greater degree with refinery operatives having clearly better control on the plant operations. Higher concentration of phenol, COD, BOD₃ and sulphide at early stages of operation was probably due the fact that the plant was still under commissioning conditions and plant operatives were streamlining the operations within the plant.

With the activation of four SBR units in April 2003, it is apparent that a better control of phenol, COD, BOD₃ and sulphide is observed in the final effluent, with lesser fluctuation in the parameter value. It should also be mentioned that although more troublesome wastewater was processed in the ETP in 2004 (as previously indicated), the final effluent values of phenol, COD, BOD₃ and sulphide were generally lower than the regulatory limit.
Fig. 5.25: Concentration of phenol, COD, BOD₅ and sulphide in the final effluent during 2000-2004.
5.4.2 Relationship Between Water Quality Parameters in the Final Effluent

In this section the determination of any functional relationship that exists between treated wastewater quality parameters in the final effluent of the ETP is investigated. The section discusses:

a. Relationship between phenol and COD/BOD$_5$/sulphides;

b. Relationship between COD and BOD$_5$.

5.4.2.1 Correlation between phenol and BOD$_5$/COD/sulphide

Correlation graphs of phenol versus BOD$_5$/COD/sulphide in the final effluent pond are shown in Figs. 5.26-5.28. The data from the final effluent include previous daily data collected during 2000 to 2004. The data were plotted for all the data sets year by year. The graphs on the top show the data of the five years with each represented as a different series. The graphs at the bottom show the data excluding those of year 2000 (the commissioning year of the plant).

It is quite clear that there is a large scatter of the data points in all graphs even when the data from first operational year were excluded. The level of scatter of data is clearly reflected by the low $r^2$ values of the linear fit as shown in Table 5.3. Nevertheless, the significance of the relationship was judged by the confidence interval of the slope (CI), such that a relationship is considered statistically significant if the slope is different from zero. Table 5.3 shows that the relationship between phenol/BOD$_5$ and phenol/COD are considered significant but weak while that between phenol and sulphide is not significant.
Table 5.3: Relationships between phenol and other water parameters based on daily data from final effluent pond readings

<table>
<thead>
<tr>
<th>Relationship</th>
<th>Linear Equation</th>
<th>$r^2$</th>
<th>Confidence Interval of the slope (CI)</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data 2000-2004 BOD₅-Phenol</td>
<td>$\text{BOD}_5 = 31.152 \times \text{Phenol} + 13.63$</td>
<td>0.1135</td>
<td>$31.152 \pm 6.05$</td>
<td>5.26 top</td>
</tr>
<tr>
<td>Data 2001-2004 BOD₅-Phenol</td>
<td>$\text{BOD}_5 = 16.859 \times \text{Phenol} + 13.17$</td>
<td>0.1028</td>
<td>$16.859 \pm 4.65$</td>
<td>5.26 bottom</td>
</tr>
<tr>
<td>Data 2000-2004 COD-Phenol</td>
<td>$\text{COD} = 49.216 \times \text{Phenol} + 75$</td>
<td>0.1017</td>
<td>$49.216 \pm 7.94$</td>
<td>5.27 top</td>
</tr>
<tr>
<td>Data 2001-2004 COD-Phenol</td>
<td>$\text{COD} = 65.5 \times \text{Phenol} + 67.2$</td>
<td>0.0809</td>
<td>$65.5 \pm 14.45$</td>
<td>5.27 bottom</td>
</tr>
<tr>
<td>Data 2000-2004 Sulphide-Phenol</td>
<td>$\text{Sulphide} = 0.85 \times \text{Phenol} + 0.0002$</td>
<td>0.2781</td>
<td>$0.85 \pm 0.322$</td>
<td>5.28 top</td>
</tr>
<tr>
<td>Data 2001-2004 Sulphide-Phenol</td>
<td>$\text{Sulphide} = 0.098 \times \text{Phenol} + 0.0189$</td>
<td>0.1007</td>
<td>$0.098 \pm 0.303$</td>
<td>5.28 bottom</td>
</tr>
</tbody>
</table>

Since the regulator is interested in the degree of the monthly compliance to the parameters and tolerates exceeding of regulatory values on a daily discharges, it is worth to investigate the existence of relationship between phenol and other parameters using monthly averages of the parameter values. Table 5.4 summarises these relationships.

Table 5.4: Relationships between phenol and other water parameters based on monthly average of final effluent pond readings

<table>
<thead>
<tr>
<th>Relationship</th>
<th>Linear Equation</th>
<th>$r^2$</th>
<th>Confidence interval of the slope (CI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD₅-Phenol</td>
<td>$\text{BOD}_5 = 43.7 \times \text{Phenol} + 9.7$</td>
<td>0.56</td>
<td>$43.7 \pm 15.3$</td>
</tr>
<tr>
<td>COD-Phenol</td>
<td>$\text{COD} = 68.6 \times \text{Phenol} + 71.3$</td>
<td>0.25</td>
<td>$68.6 \pm 37.25$</td>
</tr>
<tr>
<td>Sulphide-Phenol</td>
<td>$\text{Sulphide} = 1.29 \times \text{Phenol} + 0.1769$</td>
<td>0.76</td>
<td>$1.29 \pm 0.38$</td>
</tr>
</tbody>
</table>

The slopes of the relationships based on monthly averaging (Table 5.4) compare well with those based on daily analysis (Table 5.3). However, averaging dampens the scatter of the data as
reflected by the higher $r^2$ values in Table 5.4. Nevertheless, the applicability of these relationships cannot be relied upon as the effluent needs to be monitored and controlled on a daily basis. But, the relationships could be important as the regulator is also interested in the degree of the monthly compliance to the parameters and tolerates exceeding of regulatory values on a daily basis as long as the monthly averages are controlled within the acceptable limits.

If we are to consider the regulator's requirements in the final effluent as per Table 2.2, which call for 100, 20 and 0.05 mg/l for COD, BOD$_5$ and sulphides, respectively, then substitution into the established relationships for monthly average data, which are summarized in Table 5.4, shows that phenol, which is regulated at 0.1 mg/l, is the critical factor. Thus, if the COD value is 100 mg/l then phenol in the final effluent would be 0.42 mg/l which is higher than the regulator's limit. For BOD$_5$ at 20 mg/l, the phenol would be 0.24 mg/l which again is greater than the regulator's permissible limit. For sulphides at 0.05 mg/l, the phenol value would be 0.14 mg/l which is again greater than the allowable limits set by the Authority.

These relationships may be used with great caution to estimate expected conformance of parameters with regulators requirements. Generally, meeting a phenol value of 0.1 mg/l or less in the final effluent prior to discharge means that the regulatory limits for COD, BOD$_5$ and sulphides are met on a monthly average basis only. It should be further noted that although linear regression was adopted to establish relationships between phenol and other parameters, other non-linear relationships including logarithmic and power relationships were investigated but did not yield better $r^2$ values, in most cases.
Fig. 5.26: BOD$_5$ versus phenol concentration for daily final effluent data, for the years 2000 to 2004 (top) and the years 2001 to 2004 (bottom).
Fig. 5.27: COD versus phenol concentration for daily final effluent data, for the years 2000 to 2004 (top) and the years 2001 to 2004 (bottom).
Fig. 5.28: Sulphide versus phenol concentration for effluent data for the years 2000 to 2004 (top) and the years 2001 to 2004 (bottom).
5.4.2.2 Relationship between COD and BOD$_5$

Figure 5.29 shows daily variations in the BOD$_5$ versus COD for the final effluent during the years 2000-2004. The data in 2000 show very high values for both parameters (Fig. 5.29 top) as compared to data from later years due probably to plant streamlining period. Nevertheless, the amount of scatter in the data is profound in all the years.

Fig. 5.29: COD versus BOD$_5$ values recorded from the effluent pond using the daily data for the years 2000 to 2004 (top) and the years 2001 to 2004 (bottom).
Results of linear regression of the data including and excluding those of year 2000 are listed in Table 5.5. Again, the relationships are weak (low $r^2$) but statistically significant as the confidence interval of the slope does not pass through zero. The scatter in the data is again dampened by regressing monthly average data as compared to daily data. Based on the regression results it can be concluded that the effluent has a COD:BOD$_5$ ratio of about 1:1.6. The line of best fit intercepts the y-axis at a COD value of 55-58 mg/l which may be considered the non-degradable part of the organic matter in the treated effluent.

<table>
<thead>
<tr>
<th>Relationship</th>
<th>Linear Equation</th>
<th>$r^2$</th>
<th>Confidence Interval (CI)</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daily data 2000-2004 COD- BOD$_5$</td>
<td>COD$_{(t+2000)} = 1.573 \text{BOD}_5 + 58.2$</td>
<td>0.4201</td>
<td>1.573 ± 8.64x10$^3$</td>
<td>5.29 top</td>
</tr>
<tr>
<td>Daily data 2001-2004 COD- BOD$_5$</td>
<td>COD$_{(t+2000)} = 1.267 \text{BOD}_5 + 58.5$</td>
<td>0.1007</td>
<td>1.267 ± 0.000225</td>
<td>5.29 bottom</td>
</tr>
<tr>
<td>Monthly average data 2000-2004 COD- BOD$_5$</td>
<td>COD$_{(t+2000)} = 1.64 \text{BOD}_5 + 54.6$</td>
<td>0.496</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
6.1 SUMMARY AND CONCLUSIONS

Phenol is a wastewater quality parameter that the regulators closely look at while monitoring the wastes from heavy industries such as refineries. Little is known of the effectiveness of the commonly employed treatment processes for the removal of phenol from refinery wastewater in the UAE. The rationale behind this study stems from the fact that the condensate refinery (EPCL) is facing challenges to maintain a consistent standard of phenol in the final effluent of treated wastewater. The main objectives of this study were to investigate the efficiency of EPCL ETP in reduction of phenol in the refinery wastewater and to explore the potential correlation between phenol and other water quality parameters in the treated wastewater.

The adverse effects of phenols on the receiving environment have been reviewed. It is well documented that phenol and its derivatives pose danger to both humans and marine life with varying toxicities which depend on their solubility and persistence in the system. The sources and formation of phenol and its derivatives are based on many complex reactions.

This study provides an in-depth description of the unit processes in the ETP employed to treat the different waste streams generated at EPCL. To achieve the stated objectives of this study, some of the waste streams as well as the influent and effluent of each unit process at the refinery wastewater treatment plant have been characterized for phenol and other water parameters. The study has also identified the different types of phenols which are formed in the processes. The limitations of this study have been mentioned in Chapter One as referred to in the “Scope of Work”. The following conclusive remarks/observations are drawn based on the data collected in this study and those collected from the refinery testing records:
1. The processes in the refinery ETP are different in their characteristics, retention time and treatment efficiencies with the Sequencing Batch Reactors (SBR) homogenises the effluent before the final polishing steps.

2. The effluent streams going through the plant vary in their chemical characteristics over time but variations become less pronounced after the SBR.

3. Phenol in refinery wastewaters comes from different sources such as the tank water drain (condensate crude tank draws), the neutralized spent caustic waste as well as the desalter wastewater streams. The neutralized spent caustic stream, desalter wastewater stream and tank drain wastewater streams produce average annual phenol loadings of 1497.8, 131.5 and 69.3 kg, respectively. Although phenol were detected in other sources (oily water salt filter, kero water coalescer and diesel water coalescer or the flow rates of these streams provide insignificant phenol loading on the ETP.

4. The concentration of phenols in the troublesome waste streams vary significantly between certain types of phenols with phenol, m,p-cresols, o-cresol, tri and tetra-chlorophenols and to a lesser extent 4-chloro-3-cresol are common among these wastewater streams.

5. Phenol and m-p-cresols are the most dominant types in the wastewater streams.

6. The existence of 7 out of 15 phenol compounds in the troublesome waste streams is evident, indicating that these compounds are probably consistently available in the processed condensate crude oil.

7. Variations between phenol types are most significant in the tank draw wastewater due to the fact that these streams originate from streams which are affected by the type of oil in the crude oil tanks. Phenol concentrations vary between 0.63 and 330 mg/l.
8. Based on the samples collected from the effluent of the treatment processes, it is evident that odour, colour and clarity improve significantly through the stages of the treatment plant.

9. The most effective process within the ETP for the reduction of organic loading, phenols, and sulphides is the SBR.

10. Relationship between phenol concentration in the discharged final effluent and other water parameters including COD/BOD₅/sulphides are weak but statistically significant.

11. On the average, the final effluent of the ETP is characterized by a COD-to-BOD₅ ratio of about 1.6 with 55 mg/l non-degradable COD.

6.2 RECOMMENDATIONS

This study has given coverage of several aspects of the operation of the EPCL ETP but has been limited to the time and available resources. Findings of this study may be used for future research projects aimed at reduction of phenols in the effluent. It is, therefore, recommended that:

1. A detailed study comparing condensate refineries around the world may be undertaken in order to characterise the sources and quantify phenols in condensate refinery effluent treatment plants and to further investigate, phenols and other aromatic hydrocarbons are site specific or Regional/International in nature.

2. A better understanding is required of the chemicals and additives mixed with the crude condensate prior to export from the source to the refinery as this will better identify the source of phenols. This would further help in distinguishing between naturally occurring phenols and those coming in with the crude condensates as additives. Thus, a study may be conducted
through testing condensates at the point of abstraction and after three phase separation and additive addition at source.

3. The relationships between phenol and other water parameters may be investigated further to establish the process optimization. A mixing/homogenization tank or storage facility may be developed to ensure that inlet conditions are always the same to the plant and thus controlling its efficiency much more closely. Thus inlet conditions would be recorded as for outlet conditions and a comparative study can be drawn on performance of plant overall.

4. Further studies can be made on more samples targeting different condensates to evaluate the source and the level of phenol per source. The same studies could be conducted against the desalter unit whilst changing some process parameters such as the potential difference across the electro-plates or the retention time within the unit. The neutralized spent caustics could also be more closely monitored to determine how the phenols are produced in the reactions that take place prior to neutralization and transfer to the ETP.

5. Evaluation of potential relationship between COD and phenols may be done on the condensate tank water drains, desalter and neutralized spent caustic streams. Such relationships, if exist, help establish better planning for more effective treatment of the waste streams before being fed into the ETP processes.

6. Further studies may be conducted on the SBR to investigate the role of reaction cycle, reaction time, and additives concentration. A mass balance testing of the SBR would be also necessary to determine if the phenol has been fully consumed and/or to what extent absorbed by the sludge itself in the SBR.

7. Research is needed to characterise the SBR bacteria and find if there is a more effective family of bacteria for breakdown of phenols as well as the oils which flow in with the wastewater.
A further study could be undertaken to evaluate the effective conversion of phenol into derivative compounds for the different influent wastewater streams at the EPCL refinery. A similar study may be undertaken to evaluate the effective treatment of benzene, toluene and xylene in refinery wastewater using currently operating wastewater treatment plant.
LIST OF REFERENCES

1. Abu Dahah, U.M.T., Marine Pollution and methods of combat, Department of Oceanography, Faculty of Science, Alexandria & Qatar Universities, 1992 (Arabic Text).


14. ENOC, 2003 Website research on www.enoc.com;


45. Shumway D. I. Effects of effluents on flavor of salmon fish. Agricultural Experiment Station, Oregon State University, Corvallis, 1966.


49. Train R.E., Quality Criteria for Water, Environment Protection Agency, UK.


Note: Other sources include standard environmental regulations for discharge of wastewater from personnel discussions and review of refinery data available in their records.
APPENDIX ONE

PROCESS & INSTRUMENTATION DIAGRAM FOR EFFLUENT TREATMENT PLANT (ETP)

ENOC PROCESSING COMPANY LLC

DRAWING No. 22-a-10001 Rev. 6
إن العوامل الموجودة في وحدة المعالجة تتوزع من عملية التدفق الشبه مستمرة (مثل CPI, IGF جل.ا) إلى عملية تدفق مادتر من خلال ملفات تدفق المتخلف والمتبادر بسلسلة مفاعلات سريعة ذات تدفق مستمر. وتوضح الدراسة التبانيات في معايير جودة المياه في المراحل الأولى من المعالجة ولكن المياه العادية تتجاوز في (.),

وعند تجاوزها فإنها تدخل في الفلتر الترابي والكريستين.

والمياه المعالجة والنتائج عن عمليات محطة المعالجة تتسم تصنيفاً على صعيد اللون والرائحة والشفاء من خلال حفظات المعالجة (العمليات). تميز عمليات المفاعلات (معالجة بالأوكسجين الطاقم) المتواجدة والتي تعمل على دفعات خاصة بها أفلس طريقة لمعالجة الفيتنول في المياه الملوثة والأشجع العضوي بمستوى أقل عن طريق المفاعل الكريستين المزيل للمواد الصلبة العصوية الذائبة. وقد أثبتت هذه المفاعلات جدارتها بشكل متوازي في تنقيه المياه من الملوثات العضوية والكريستينية.

بناءً على تحليل المعلومات اليومية لخمس سنوات (2000-2002)، وجد أن هناك علاقة ضعيفة بين مستوى تركز الفيتنول في المياه العادية المعالجة ومستوى الحاجة إلى الأكسجين (COD) والحاجة إلى الأكسجين عضوي (BOD)...والكريستينات بالرغم من أنها قد تكون مهمة من الناحية الإحصائية في معظم الحالات.

كذلك فإن الدراسة بينت أن العلاقة فيما بين الحاجة إلى الأكسجين (COD) والحاجة إلى الأكسجين عضوي (BOD)...في المياه المعالجة النهائية تقدر بنسبة 1.6 إلى 1 ومتوسط الحاجة إلى الأكسجين غير (COD) في المحلول يقدر بحولياً 55 mg/L. ومع هذا نتائج العلاقة ضعيفة إلى حد ما نتيجة لتبعثر المعلومات التي عكستها القمية الضئيلة لمعامل الفصل.

وفي الختام، نود أن نشير إلى أن الدراسة احتوت أيضاً على مقترحات متعلقة بدراسات أخرى من شأنها أن تساهم في تغيل الهدف مثل دراسة حول مقارنة أداء محطة معالجة المياه العادية لخصائص مكثفات نفط مختلفة، دراسة في تحسين العمليات عن طريق تناول العلاقة ما بين عوامل المياه الملوثة العامة بالإضافة إلى أن استقصاءات لاحقة تهدف إلى تطوير عمليات SBR وتشمل توصيف الكريستينات الناشئة في الرواسب الطينية تأتي في توسعتها متوجة بدراسة أداء محطة معالجة المياه الملوثة العامة المتعلقة بالإزالة آثار التلوث الهيدروكربوني العظيقي.
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جامعة الجوف
تقييم فعالية تقنيات التحكم في التلوث لتقليل تركيز الفينول في محطة معالجة المياه العادية الناتجة عن تكرير النفط لدى شركة إينوك.

رسالة مقدمة من الطالب

وضاح شهاب محمد عيد غانم الهاشمي

رسالة مقدمة إلى

جامعة الإمارات العربية المتحدة

استكمالاً لمتطلبات الحصول على درجة الماجستير في علوم البيئة

2006