Effluent Wastewater Analysis in a Typical Crude Oil Refinery:

A case Study of Khartoum Refinery, Sudan

Samahir Hassan Eljozoli Hajomer

B.Sc. (Honors) in Chemical Engineering Technology, University of Gezira
(2014)

A Dissertation
Submitted to the University of Gezira in Partial Fulfillment of the
Requirements for the Award of the Degree of Master of Science

in

Chemical Engineering

Department of Chemical Engineering and Chemical Technology
Faculty of Engineering and Technology

August, 2016
Effluent Wastewater Analysis in a Typical Crude Oil Refinery:

A case Study of Khartoum Refinery, Sudan

Samahir Hassan Eljozoli Hajomer

Supervision Committee:

<table>
<thead>
<tr>
<th>Name</th>
<th>Position</th>
<th>Signature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. Hamid Mohamed Mustafa</td>
<td>Main Supervisor</td>
<td>……………………..</td>
</tr>
<tr>
<td>Dr. Mohamed Osman Babiker</td>
<td>Co- Supervisor</td>
<td>……………………..</td>
</tr>
</tbody>
</table>

Date of Examination : August / 2016
Effluent Wastewater Analysis in a Typical Crude Oil Refinery:

A case Study of Khartoum Refinery, Sudan

Samahir Hassan Eljozoli Hajomer

Examination Committee:

<table>
<thead>
<tr>
<th>Name</th>
<th>Position</th>
<th>Signature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prof. Hamid Mohamed Mustafa</td>
<td>Chair Person</td>
<td>..</td>
</tr>
<tr>
<td>Dr. Bashir Mohamed Al Hassan</td>
<td>External Examiner</td>
<td>..</td>
</tr>
<tr>
<td>Dr. Magdi Ali Osman</td>
<td>Internal Examiner</td>
<td>..</td>
</tr>
</tbody>
</table>

Date of Examination : 16 / 8 / 2016
بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

قال تعالى:

﴾وَلَّا تَفْسِدُوا فِي الْأَرْضِ بَعْدَ إِصْلَاحِهَا وَادْعُوهُ خَوْفًَا وَطَمَعًا ۚ إِنَّ رَحْمَتَ اللَّهِ قَرِيبٌ مِّنَ المُحْسِنِينَ (56)﴾

صدق الله العظيم

الاعراف الآية:56
Dedication

To my angel, to the true meaning of love and compassion, who
her love and prayers was the reasons to success, my mother. I
dedicate this work also to my dearest husband.
To whom I learned with them the true meaning of friendship
and loyalty, which I found and knew I shouldn't let go of them,
to whom I shared the pain and the joy of the journey and
helped me to be stronger to my
family and friends.
To who guided me the whole way with his knowledge and
mind, to the person whom helped me through this and was
generous with their time and advices to my respect
teacher.
Acknowledgements

First of all, I thank to God (Alla), the almighty, for giving me strength to help me to complete this research of master degree.

My thanks and gratitude to my mother, my husband and all of my family and friends who supported me to present this thesis in its final format.

I would like to express my appreciation to supervisor:

Prof. Hamid Mohamed Mustafa.

Thanks are also due to The Deputy General Manager Of Khartoum Refinery Company, to all those working in water treatment unit as well as water laboratory.

Special thanks to the Unit Assistant Engineer: Iswa Mahdi & Nasr Fadlallah.

Finally thanks to whoever gave me a hand of help.
Effluent Wastewater Analysis in a Typical Crude Oil Refinery

A case study: Khartoum Refinery Company (KRC)

Candidate Name: Samahir Hassan Eljozoli Hajomer

ABSTRACT

The chemical and/or microbial contamination of wastewater of oil refineries is an environmental hazard. The KRC produces large amounts of wastewater that requires treatment. These waters come from many units in the refinery such as distillation columns, heat exchangers and the desalting unit. All the wastewaters from the different sources are collected together and then sent to the, Physical Treatment unit, chemical treatment. And then the Biological Treatment unit. The objective of this study is the physical, chemical and biological analysis of waste water. Investigation of wastewater in the refinery and associated pollution problems, review of the treatment processes of the refinery, Analysis and comparison of treated waste water properties with local and international specifications. The methods used in this study were standard tests used in Khartoum Refinery Company to test pH, COD, BOD, Phenol Content, Oil content, NH₃-N and Suspended Solids Sulfide Content. The results of these laboratory tests were pH before treatment 7.84, after treatment 7.75, COD before treatment 2153.93 mg/l, after treatment 150.8 mg/l, BOD before treatment 210.92 mg/l, after treatment 21.92 mg/l, Phenol Content before treatment 70.76 mg/l, after treatment 0.19 mg/l, Oil Content before treatment 584.50 mg/l, after treatment 16.39 mg/l, Sulfide Content before treatment 0.53 mg/l, after treatment zero. The results of this study were then studied, analyzed and compared to the local Sudanese Standards as well as to the International Standards. From the analysis testes it is found that the pH, BOD, Sulfide content of the wastewater are matching the Sudanese Specification (174 / 2008 ) and International Standards, while the phenol content(0.19) is not conforming of the Sudanese Standards(0.001) and oil content value (16.39 mg/l)is not conform to that of the Sudanese Specifications(10 mg/l). It also found that the COD (150.8 mg/l) was above the International Standards(125 mg/l). and the Oil Contents(16.36 mg/l) were above the International Standards (10 mg/l). It may be concluded that some of the studied pollutants were within the range of Sudanese and International specifications, while the others high. After this study and analysis it is recommended to add more processing units such as membrane separation processes, to treat the water so as to meet the specification requirement.
تحليل المياه العادمة من مصفاة لتكريير النفط - دراسة حالة: شركة مصفاة الخرطوم

اسم الدارس: سماهر حسن الجزولي حاج عمر

ملخص الدراسة

يعتبر التلوث الكيميائي والميكروبي من أكثر المشاكل التي تواجه الإنسان أشدّ أضرارًا على صحة الإنسان والحيوانات، وجميع المخلفات ذات النزعة الاصطناعية الأخرى. تُعد هذه الدراسة دراسة حالةً في شركة مصفاة الخرطوم حيث وجدنا أن هناك مقايير كبيرة من المياه المستخدمة في المصفاة مثل مادة التبريكي ومعالجات المياه وغيرها تكون عبارة عن مادة مغذية للكثير من التلوث بعد الاستخدام. تأتي هذه المياه من عدة وحدات داخل المصفاة مثل وحدة إزالة الملوحة وأبراج التقطير والعمليات الحرارية. تم تجميع كلي هذه المياه العادمة وتم نقلها إلى وحدات المعالجة الفيزيائية، ثم إلى وحدة المعالجة الكيمياوية، ثم إلى وحدة المعالجة البيولوجية. يهدف من هذه الدراسة إجراء التحليل الفيزيائي والكيمياوي والبيولوجي، ثم التحقق من نسبة ماء الصرف الصحي في مصانع البتروكي ونلاحظ جليًا كيف أن مشاكل التلوث وكذلك استعراض عملية المعالجة في المصفاة وراءها "مقارنة النتائج للمادة المعالجة ومقارنتها مع المواصفات السودانية والعالمية. الطرق المستخدمة في هذا البحث تم إجراء التحليل الفيزيائي والكيمياوي بالاعتماد على المصفاة وفقاً للطرق العلمية المعيارية. تم تحديد كل من الخصائص التالية: الرقم الهيدروجيني قبل المعالجة يساوي 7.84 ودورة المعالجة يساوي 7.75، المواد الصناعية الدقيقة بعد المعالجة تساوي 51 ملم/متر، الأمونيا قبل المعالجة 15.41 ملم/متر، وبعد المعالجة تساوي 4.58 ملم/متر، محتوى الزيت قبل المعالجة يساوي 58.50 ملجم/متر، و بعد المعالجة يساوي 16.39 ملجم/متر، محتوى الفينول قبل المعالجة يساوي 7.06 ملجم/متر، و بعد المعالجة يساوي 0.19 ملجم /متر، قبل المعالجة يساوي 2153.93 ملجم /متر بعد المعالجة يساوي 150.8 ملجم/متر، درجة BOD: 21.92 ملجم/متر، محتوى الكيروس قبل المعالجة يساوي 4.53 ملجم/متر، و بعد المعالجة يساوي 0.19 ملجم /متر بعد المعالجة يساوي 0.001 ملجم/متر، بالنسبة للمؤلفة كما تم تقصي الفحص المائي للمؤلفات العالمية حيث وجد أن طلب الأوكسجين الكيميائي غير مطابق للمؤلفة حيث كانت قيمته 150.80 ملجم/متر وقيمة المؤلفة 125 ملجم/متر. خلاصة القول أن بعض الفحوصات تقع ضمن المواصفات العالمية والسودانية ولكن البعض الآخر خارج منها. لذلك أوصي هذه الدراسة لإضافة وحدات معالجة أخرى كالفصل عن طريق الأغشية حتى تكون المياه مطابقة للمؤلفات المطلوبة ولا تسبب أي تلوث".

8
TABLE OF CONTENTS

VERSE .......................................................................................................................... I
DEDICATION .............................................................................................................. II
ACKNOWLEDGMENTS ............................................................................................... III
ABSTRACT (ENGLISH) .............................................................................................. IV
ABSTRACT (ARABIC) ............................................................................................... V
TABLE OF CONTENTS ......................................................................................... VI

LIST OF TABLES ........................................................................................................ IX

LIST OF FIGURES ..................................................................................................... X

ABBREVIATIONS ..................................................................................................... XI

CHAPTER ONE: INTRODUCTION
1:1 General introduction .......................................................................................... 1
  1.1.2 Refinery Wastewater ................................................................................. 2
  1.1.3 Sour Water in the Refinery ................................................................. 3
  1.1.4 Naphthenic Acids ................................................................................... 3
1.2 Objectives of the Study .................................................................................. 5

CHAPTER TWO: LITERATURE REVIEW
2.1 Introduction ..................................................................................................... 6
2.2 Method of Waste Water Treatment ............................................................ 6
2.3 General Method of Waste Water Treatment in Chemical Plants ......................... 8
2.4 Method of Waste Water Treatment Petroleum in Refineries ......................... 9
2.5 Equipment Used in Wastewater Treatment Plants ...................................... 9
  2.5.1 Trickling Filter ....................................................................................... 9
  2.5.2 Rotating Biological Contactor ............................................................. 13
2.5.3 Activated Sludge Process

2.6 Water and Wastewater in Khartoum Refinery

2.7 Classification of Refinery Wastes

2.7.1 Wastewater Types

2.7.2 Air Emissions

2.7.3 Residuals Types

2.8 Quantification of Waste Discharges

2.8.1 Air Emissions

2.8.2 Wastewater

2.9 Treatment Technologies for Petroleum Refinery Effluents

2.10 Effluent Treatment Methods

2.10.1 Physical Treatment

2.10.2 Chemical Treatment

2.10.3 Biochemical Unit Processes

2.11 Sludge Treatment

2.12 Oily Waste Water Treatment Units

2.13 Sour Water Treatment

2.13.1 Design Basis of the Sour Water Unit

2.14 Oxidation Ponds
CHAPTER THREE: MATERIALS AND METHODS

3.1 Introduction ...........................................................................................................43
3.2 The Materials .......................................................................................................43
3.3 Test Methods .......................................................................................................44
   3.3.1 Test Method for Ammonia Nitrogen ...............................................................44
   3.3.2 Test Method for pH value ..............................................................................46
   3.3.3 Test Methods for Chemical Oxygen Demand ..............................................47
   3.3.4 Test Methods for Sulfide ..............................................................................48
   3.3.5 Test Methods for Oil Content ......................................................................51

CHAPTER FOUR: RESULTS AND DISCUSSIONS

4.1 Results ..................................................................................................................54
4.2 Environmental Regulations ...............................................................................56
4.3 Discussion ............................................................................................................60

CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion ...........................................................................................................61
5.2 Recommendations .............................................................................................61

REFERENCES ............................................................................................................62

APPENDIXES

Appendix (A) ..........................................................................................................64
Appendix (B) ..........................................................................................................65
Appendix (C) ..........................................................................................................66
### LIST OF TABLES

Table 2.1: Air Pollutants Produced By Oil Refinery ................................................. 21

Table 2.2: waste water treatment levels and process .............................................. 28

Table 2.3: The performance index of this system is as following ............................. 37

Table 4.1: Result of Analysis of Wastewater before treatment ............................... 54

Table 4.2: Analysis Results of Treated Wastewater ............................................. 55

Table 4.3: Average Analysis of Water Samples for the period 1st of February to 30 of March 2016 ............................. 56

Table A: Sudanese Limits for Industrial Effluents Discharge (standard 174/2008-liquid industrial waste) ................................................................. 64

Table B: World Bank Limits for Direct Discharges of Treated Industrial Effluents to Surface Water ................................................................. 65

Table C1: pH values compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining ................................................................. 66

Table C2: COD mg/l compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining .................................................. 66

Table C3: Oil Content mg/l compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining ................................................................. 66

Table C4: Phenol Content mg/l compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining .................................................. 67

Table C5: Sulfide Content mg/l compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining ................................................................. 68

Table C6: Ammonia Nitrogen mg/l analysis results .................................................. 68
LIST OF FIGURES

Figure 1.1: Process Flow diagram of Oily waste water treatment process ........................................2

Figure 2.1: Schematic diagram of a complete trickle filter system .................................................10

Figure 2.2: Schematic diagram of a rotating biological contactor (RBC) ........................................13

Figure 2.3: Activated sludge process .........................................................................................16

Figure 2.4: The Refinery Sludge paths ......................................................................................20

Figure 2.5: Waste Water Treatment Process .............................................................................24

Photo 2.6: Schematic diagram of sequence for treating petroleum refinery effluent ..............25

Figure 2.7: KRC Biological treatment ......................................................................................36

Figure 2.9: Sour water stripper process flow diagram ..............................................................41

Figure 2.8: Oxidation pond Khartoum Refinery ........................................................................42

Figure 4.1: pH compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining .........................................................56

Figure 4.2: COD compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining .........................................................56

Figure 4.3: Oil Content compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining .........................................................57

Figure 4.4: Phenol Content compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining .........................................................57

Figure 4.5: Sulfide compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining .........................................................58

Figure 4.6: Ammonia Nitrogen compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining .........................................................58
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAF</td>
<td>Dissolved Air Floatation</td>
</tr>
<tr>
<td>BOD&lt;sub&gt;5&lt;/sub&gt;</td>
<td>Biochemical Oxygen Demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>DCU</td>
<td>Delayed Coker Unit</td>
</tr>
<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>TOD</td>
<td>Total oxygen Demand</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>RBC</td>
<td>Rotating Biological Contactor</td>
</tr>
<tr>
<td>TF</td>
<td>Trickling Filter</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td>TPH</td>
<td>Total petroleum Hydrocarbon</td>
</tr>
<tr>
<td>O &amp; G</td>
<td>Oil and Grease</td>
</tr>
<tr>
<td>KRC</td>
<td>Khartoum Refinery Company</td>
</tr>
<tr>
<td>DGF</td>
<td>Dissolved Gas Floatation</td>
</tr>
<tr>
<td>CASS</td>
<td>Cycle Activated Sludge System</td>
</tr>
<tr>
<td>HDS</td>
<td>Hydrodesulphurization</td>
</tr>
<tr>
<td>RFCC</td>
<td>Residual Fluid Catalytic Cracking</td>
</tr>
<tr>
<td>GDHT</td>
<td>Gasoline / Diesel Hydro Treating</td>
</tr>
<tr>
<td>SWS</td>
<td>Sour Water Stripping</td>
</tr>
<tr>
<td>WGS</td>
<td>Waste Gas Sweetening</td>
</tr>
<tr>
<td>CWR</td>
<td>Condensate Water Recovery</td>
</tr>
</tbody>
</table>
CHAPTER ONE

Introduction

1.1 General

Nowadays the industries must face the challenge of designing cleaner products and processes, because of environmental regulations and requirements of sustainable development. Along the lines of reducing pollution and increasing profits simultaneously, process design has evolved incorporating sustainability goals and minimizing environmental impacts. [1]

Petroleum wastewater from refineries contains high levels of pollutants and is characterized by the presence of large quantities of refinery effluent such as oil products and chemicals that are hard to degrade. Regulatory authorities deny permits to discharge this petroleum wastewater to maintain the chemical, physical and biological integrity of the fresh water resources.

With rising crude prices and depleting quality of crude, however, the level of wastewater pollutants in petroleum wastewater has increased. Such conditions are forcing refineries to use a more advanced water treatment, water recovery methods, and robust processes that work well under a variety of conditions and can handle the changing refinery effluent flow rates. A process that is economical is needed to make all of this feasible [2].

Petroleum refineries process crude oil into refined products, such as gasoline, diesel and kerosene. Refining processes use large quantities of water, primarily for, desalting and cooling thus generating waste streams, that are combined and carried to the refinery wastewater treatment plant. Many wastewater pollutants are easily removed by the refinery wastewater treatment plant; however, some pollutants remain in process waters such as naphthenic acids (NAs), these are more difficult to treat and create operational problems, such as corrosion and toxicity.

Activated sludge systems are common biological treatment processes used to treat refinery wastewaters; however, very limited information exists relative to the fate. And effect of NAs in refinery activated sludge units and whether such treatment systems are capable of reducing the effluent NA concentration. [3]
1.1.2 - Refinery Wastewater:

The oily waste water from crude oil tanks is mixed with fresh water and are pumped into oil separator where the most of floating oil will be separated from water by gravity effect. Then it flows into two stages Dissolved Air Floatation ponds (DAF) to eliminate remaining emulsified oil. Afterwards, it is sent to the biochemical reaction ponds where most of organic pollutants such as BOD/COD are biodegraded. And through nitrification and de-nitrification effects, a part of ammonia is turned into nitrogen to atmosphere. Finally, it enters sedimentation ponds where water and activated sludge are separated. The oily slurry from oil separator, dissolved air flotation ponds and the remained activated sludge from biological reaction system are dewatered by a centrifuge. The waste oil is recycled to the DCU unit and the treated waste water is discharged into oxidation ponds. The water in oxidation ponds is used for irrigation and remainder is discharged to evaporate.

The refinery process flow diagram of oily waste water treatment process is shown in figure 1.1

![Figure 1.1 Process Flow diagram of oily waste water treatment process(KRC EFLL-PLANT)](image-url)
1.1.3- **Sour water in the Refinery:**

Sour water is any water from a refinery that contains hydrogen sulphide. In addition, sour water may contain ammonia, light hydrocarbons, phenol and cyanide.

The sour water producing sources:

Atmospheric Crude, catalytic cracking and reforming, Delayed Coker Unit( DCU) distillation column produce sour water as condensates from steam used in injection and stripping removed by overhead condensing system. Another source of sour water is the hydro-treater wash water.

**Sour Water Process Description:**

There are four processing steps in sour water treatment these are [4]:

1. Degassing.

2. De-oiling and feed storage.


4. Sour gases incineration.

1.1.4-Naphthenic Acids :

Naphthenic acids are a mixture of cyclo-paraffins with alkyl side chains ending with a carboxlic group. These compounds are normally found in middle distillates such as kerosene and gas oil.

High boiling naphthenic acids from the lube oils are monocarboxylic acids,(C_{14}- C_{19}) with an average of 2.6 rings.

Naphthenic acids are classified as carboxylic monoacids of the general formula RCOOH, where Represents any cycloaliphatic structure. Generally, the term “naphthenic acid” is used to account for all carboxylic acids present in crude oil including acyclic and aromatic acids. Nearly all crude oils contain some naphthenic acids. Heavy crudes from geologically young formations have the highest acids content while paraffinic crudes usually have low acid content.[ 5 ]
Naphthenic acids constitute about 50 wt% of the total acidic compounds in crude oils. Naphthenic-based crudes contain a higher percentage of naphthenic acids. Consequently, it is more economical to isolate these acids from naphthenic-based crudes.

About 24% of naphthenic acids from middle distillates is removed by extraction with 7-10% caustic solution. The formed sodium salts, which are soluble in the lower aqueous layer, are separated from the hydrocarbon layer and treated with a mineral acid to spring out the acids. The free acids are then dried and distilled. Using strong caustic solution for the extraction may create separation problems because naphthenic acid salts are emulsifying agents.
1.2 Objectives of the Study

1- Investigate of wastewater in the refinery and associated pollution problems.

2- Review of the treatment processes in the refinery.

3- Physical, chemical and biochemical analysis of waste water

4- Analysis and compare of treated waste water properties with local and international specifications.
CHAPTER TWO

Literature Review

2.1 Introduction

Wastewater is not just sewage. All the water used in the home that goes down the drains or into the sewage collection system is wastewater. This includes water from baths, showers, sinks, dishwashers, washing machines, and toilets. Small businesses and industries often contribute large amounts of wastewater to sewage collection systems; others operate their own wastewater treatment systems. In combined municipal sewage systems, water from storm drains is also added to the municipal wastewater stream. The average American contributes 265-568 liters (66 to 192 gallons) of wastewater each day. Wastewater is about 99 percent water by weight and is generally referred to as influent as it enters the wastewater treatment facility. “Domestic wastewater” is wastewater that comes primarily from individuals, and does not generally include industrial or agricultural wastewater. At wastewater treatment plants, this flow is treated before it is allowed to be returned to the environment, lakes, or streams. There are no holidays for wastewater treatment, and most plants operate 24 hours per day every day of the week. Wastewater treatment plants operate at a critical point of the water cycle, helping nature defend water from excessive pollution. Most treatment plants have primary treatment (physical removal of floatable and settle able solids) and secondary treatment (the biological removal of dissolved solids). [6]

2.2 Method of Waste Water Treatment

Wastewater is characterized in terms of its physical, chemical and biological constituents. The strength of waste water is normally measured using accurate analytical techniques. The more common analyses used to characterize waste water entering and leaving a plant are:

• BOD5, COD, TSS, pH, Total Phosphorus, Total Nitrogen.

(i) **Biochemical Oxygen Demand (BOD):** BOD is the amount of oxygen used by organisms while consuming organic matter in a waste water sample. It is possible to
assess the performance of a waste water treatment plant by measuring the BOD5 of the inflow and the outflow. Many factors can influence this test, such as temperature of incubation, dilution rate, nitrification, toxic substances, nature of bacterial seed and presence of anaerobic organisms. The method of measurement for the BOD5 test requires:

That the sample is homogenized, unfiltered and undecanted; and that a nitrification inhibitor is added.

The BODs test can be replaced by another parameter, total organic carbon (TOC) or total oxygen demand (TOD) if a relationship can be established between BOD5 and the substitute parameter

(ii) **Chemical Oxygen Demand (COD):** The COD test uses the oxidizing agent potassium dichromate to oxidize organic matter in the sample. The test is extensively used because it takes less time (about 3 hours) than other tests such as the BOD5, which takes 5 days. The COD test does not, however, differentiate between biodegradable and non-biodegradable organic matter.

For municipal waste water it is generally possible to establish a relationship between COD and BOD. Once a correlation has been established, the COD test can be a very useful indicator for the operation and control of the plant.

(iii) **Total Suspended Solids (TSS):** This is the sum of the organic and inorganic solids concentrations and can be subdivided into:

A- **Suspended Solids:** which represent the solids that are in suspension in the water. Generally comprised of 70% organic and 30% inorganic solids and can be removed by physical or mechanical means.

B- **Organic Solids:** about 50% of solids present in urban waste water derive from the waste products of animal and vegetable life. Sometimes is called the combustible fraction or volatile solids as these can be driven off by high temperature.

C- **Inorganic Solids:** these substances are inert and are not subject to decay. Include sand, gravel and silt.
D- Settleable Solids: this is a subset of suspended solids and represents that fraction of suspended solids that will settle in a given period, these refer to solids that are not truly dissolved and yet do not settle readily. They tend to refer to organic and inorganic solids that rapidly decay. Dissolved solids refer to that fraction of solids that pass through a 0.45 jim filter paper substitute parameter. [7]

2.3 General Method of Waste Water Treatment in Chemical Plants

The chemical industry is of importance in terms of its impact on the environment. The wastewaters from this industry are generally strong and may contain toxic pollutants.

Chemical industrial wastes usually contain organic and inorganic matter in varying degrees of concentration. It contains acids, bases, toxic materials, and matter high in biological oxygen demand, color, and low in suspended solids. Many materials in the chemical industry are toxic, mutagenic, carcinogenic or simply hardly biodegradable.

Surfactants, emulsifiers and petroleum hydrocarbons that are being used in chemical industry reduce performance efficiency of many treatment unit operations. The best strategy to clean highly contaminated and toxic industrial wastewater is in general to treat them at the source and sometimes by applying onsite treatment within the production lines with recycling of treated effluent. Since these wastes differ from domestic sewage in general characteristics, pretreatment is required to produce an equivalent effluent. In chemical industry, the high variability, stringent effluent permits, and extreme operating conditions define the practice of wastewater treatment. Proposed concept to select the appropriate treatment process for chemical industrial wastewater based on molecular size and biodegradability of the pollutant

Chemical industrial wastewater can be treated by some biological oxidation methods such as trickling filters, rotating biological contactor (RBC), activated sludge, or lagoons. Pollutants with a molecular size larger than 10,000-20,000, can be treated by coagulation followed by sedimentation or flotation.

Waste minimization in the production process in chemical industry is the first and most important step to avoid waste formation during the production. Because of the fluctuation in the
strength and flow rate, dynamic simulation is applied to chemical-industry wastewater treatment to manage and control the treatment plants [8].

2.4 Methods of Waste Water Treatment in Petroleum Refineries

The oily waste water from crude oil tanks and life water are pumped into oil separator where the most of floating oil will be separated from water by gravity effect. Then it flows into two stages Dissolved Air Floatation ponds (DAF) to eliminate remaining emulsified oil. Afterwards, it moves into biochemical reaction ponds where most of organic pollutants such as BOD/COD are biodegraded. And through nitrification and de-nitrification effects, a part of ammonia is turned into nitrogen to atmosphere. Finally, it enters sedimentation ponds where water and activated sludge are separated. The oily slurry from oil separator, dissolved air flotation ponds and remained activated sludge from biological reaction system is dewatered by a centrifuge. The waste oil from this plant is recycled to the DCU unit. The treated waste water is discharged into oxidation ponds.

2.5 Equipment Used in Wastewater Treatment Plants

2.5.1 Trickling Filter

A trickling filter (TF) is a wastewater treatment system that biodegrades organic matter and can also be used to achieve nitrification. The wastewater trickles through a circular bed of coarse stones or plastic material. A rotating distributor (a rotating pipe with several holes across it) evenly distributes the wastewater from above the bed. The microorganisms in the wastewater attach themselves to the bed (also known as the filter media), which is covered with bacteria. The bacteria break down the organic waste and remove pollutants from the wastewater. When excess nutrients became a concern, it became necessary to adapt “conventional” sewage treatment systems to meet the increased oxygen demand placed on receiving waters by high ammonia nitrogen concentrations in wastewater effluents. TFs and other attached-growth processes proved to be well-suited for the removal of ammonia nitrogen by oxidizing it to nitrate nitrogen (nitrification). [9]
When choosing an appropriate trickling filter system for a site, you must consider several components: the area and volume of the filter surface; the type of media; the size of the pump; and the requirements for operating the trickling filter.

Trickling filters can handle from 25 to 100 gallons of wastewater per square foot of filter surface per day. They are usually designed to treat 50 gallons per square foot per day.

The amount of biological material that a treatment system can handle per day is called the organic loading rate. For trickling filters, it is measured in pounds of BOD$_5$ per day per cubic foot. The organic loading rate for a trickling filter is generally from 0.005 to 0.025 pounds of BOD$_5$ per day per cubic foot of media.

The depth of the bed of media for trickling filters can vary. The deeper a trickling filter’s media, the more BOD$_5$ it can handle per day. Community-scale trickling filters range from 3 to 8 feet deep. A home-scale trickling filter can be 2 to 3 feet deep. The depth chosen depends on the amount and strength of wastewater the system is expected to handle per day.

The media in the trickling filter should be a porous material such as rock or plastic. It should have a large surface area with large openings to allow the biological material to have good...
aeration. The large openings also enable the biological material to flow to the bottom of the filter after it falls off the media so that it can exit into the clarifier/dosing tank.

The pump should be elevated above the bottom of the clarifier/dosing tank to ensure that clear water can circulate to the trickling filter. The pump requires little horsepower because it lifts the water only from the clarifier/dosing tank to the top of the trickling filter, about 10 feet.

The flow rate for the pump can be fairly low, about 3 gallons per minute, depending on the dosing rate and the surface area of the filter. A valve on the pipe entering the top of the trickling filter allows the pump flow to be adjusted.

The wastewater must be distributed evenly over the media so that it can flow in a thin film down through the media. The water can be sprayed over the top of the media or channeled through a pipe and dropped onto a splash plate, which is a plastic or fiberglass plate lying on top of the media.

Dosing to the trickling filter can be continuous, or controlled with a timer. If the flow is continuous, the rate should be fairly low, about 3 gallons per minute, to allow the biological material that falls off the media to settle in the clarifier/dosing tank. If the flow is timer-controlled, the system should be dosed often enough to prevent the biological material from drying out.

The pump should be connected to an on-off float in case the flow of water is interrupted. Without an on-off float, the pump will run with no water in the tank if flow is disrupted from the home (such as when the family goes on vacation) and the water evaporates from the trickling filter, thus reducing the volume of water in the clarifier/dosing tank.

Advantages of the Trickling Filter: [10]

- Simple, reliable process that is suitable in areas where large tracts of land are not available for a treatment system
- May qualify for equivalent secondary discharge standards
- Effective in treating high concentrations of organic material depending on the type of media used
• Appropriate for small- to medium-sized communities and onsite systems
• High degree of performance reliability
• Ability to handle and recover from shock loads
• Durability of process elements
• Relatively low power requirements
• Level of skill and technical expertise needed to manage and operate the system is moderate

Disadvantages of the Trickling Filter: [11]

• Additional treatment may be needed to meet strict discharge standards
• Generates sludge that must be treated and disposed of
• Regular operator attention needed
• Relatively high incidence of clogging
• Relatively low loadings required depending on the media
• Limited flexibility and control in comparison with activated sludge processes
2.5.2 Rotating Biological Contactor (RBC)

Is a biological treatment process used in the treatment of wastewater following primary treatment. The primary treatment process removes the grit and other solids through a screening process followed by a period of settlement. The RBC process involves allowing the wastewater to come in contact with a biological medium in order to remove pollutants in the wastewater before discharge of the treated wastewater to the environment, usually a body of water (river, lake or ocean). A rotating biological contactor is a type of secondary treatment process. It consists of a series of closely spaced, parallel discs mounted on a rotating shaft which is supported just above the surface of the waste water. Microorganisms grow on the surface of the discs where biological degradation of the wastewater pollutants takes place.[12]

Photo (2.1) Schematic diagram of a rotating biological contactor (RBC)
Advantages and Disadvantages of RBC

(i) Advantages

These advantages include:

- The elimination of the rotating distributor. Since there are less mechanical components, less money and time is required for proper upkeep.
- The elimination of ponding on the media. Increased flows do not create a ponding bottleneck as happens in trickling filters. The flow passes through the media.
- Ponding is the term used to describe what happens when water collects and accumulates on a surface to the point where it creates large puddles, or ponds.
- More uniform rotation of the media. Drives offer better control of rotation as compared to the hydraulic push of a trickling filter.
- Lack of anaerobic conditions. Since the media biofilm is constantly exposed to atmospheric air during the rotation of the drum, anaerobic conditions are typically not a concern.
- Saves space within a wastewater treatment plant. Due to the rectangular configuration of RBC basins, one unit can be located close to or possibly against another RBC unit. This may not be possible for circular shaped trickling filters.
- Reduces the problem with nuisance filter fly populations through the use of a cover. The cover also minimizes the loss of heat in the winter.
- A trickling filter requires either in-plant pumping or a steep hydraulic grade line so the wastewater can pass through each treatment unit; however, a RBC may not require inter-unit pumping for the forward flow. This can be important if a wastewater treatment plant is being upgraded minimal head loss is required.

(ii) Disadvantages

- **Lack of Flexibility** Lack of flexibility becomes a problem because of the absence of provisions for recirculation. Recirculation of secondary clarifier effluent is necessary to
maintain constant flow through the RBC to keep the biofilm submerged for a sufficient period of time.

- **Sensitivity to Industrial Wastes** Since all microorganisms used for stabilizing the waste, known as the biomass, are attached to the media in the RBC, incoming wastewater that contains a toxic substance can potentially wipe out the entire biological population when it enters the RBC.

Other treatment processes, such as the activated sludge process, constantly re-circulate the biomass into the contact tank. Since only a portion of the total biomass is ever in contact with the incoming waste stream at any given time, a toxic substance would only affect a portion of the biomass population.

- **Possible Low Dissolved Oxygen** Possible low dissolved oxygen due to high organic loadings. Dissolved oxygen is provided to the micro-organisms in the media when the media is rotated out of the waste stream and into the atmosphere. Dissolved oxygen transfer efficiency through this type of system is not especially efficient. If needed due to high organic loadings, additional dissolved oxygen cannot easily be provided to the microorganisms.

2.5.3 Activated Sludge Process.

The activated sludge process has the advantage of producing a high quality effluent for a reasonable operating and maintenance costs.

The activated sludge process uses microorganisms to feed on organic contaminants in wastewater, producing a high-quality effluent. The basic principle behind all activated sludge processes is that as microorganisms grow, they form particles that clump together. These particles (floc) are allowed to settle to the bottom of the tank, leaving a relatively clear liquid free of organic material and suspended solids. The screened wastewater is mixed with varying amounts of recycled liquid containing a high proportion of organisms taken from a secondary clarifying tank, and it becomes a product called mixed liquor. This mixture is stirred and injected with large quantities of air, to provide oxygen and keep solids in suspension. After a period of
time, mixed liquor flows to a clarifier where it is allowed to settle. A portion of the bacteria is removed as it settles, and the partially cleaned water flows on for further treatment.[13]

The resulting settled solids, the activated sludge, are returned to the first tank to begin the process again.

![Activated Sludge Process Diagram]

**Figure (2.3) Activated sludge process**

2.6 Water and Wastewater in Khartoum Refinery

2.6.1 Water in Khartoum refinery is divided into two main categories, A and B.

- **A**- 1- Water contaminated with oil.
  2- Oil contaminated with water.

- **B**- 1- Domestic wastewater.
  2- Cooling water blowdown.

The Water usage in the refinery is for the following purposes:
1- Cooling
2- Steam generation.
3- Oil washing.
4- Domestic use.
5- Fire fighting.

2.6.2 It is to be noticed that sometime the quality of the refinery discharged effluents can exceed the Sudan discharged waster quality limitations, leading to harmful environmental impact.

The location of KHARTOUM refinery along the Nile river in Sudan is just downstream of the industrial complex.

The Wastewater treatment plant is the main environment protection facility to degrade pollutants in water. The capacity is 300t/h. The quantity of coming water from the refinery/day = 11040 t/day.

The oily water from processing units is pumped into an oil separator then to the first stage and second stage floating pools to remove surface oil and other pollutants. After that it enters the biological pool to remove phenol contaminants. Finally it is now allowed to enter into discharge pool.

2.6.3 Wastewater Lagoons

Khartoum Refinery Company limited built three lagoons to treat wastewater from treatment plant and production wastewater. Wastewater in lagoon would not be discharged and leak but vaporized. The total capacity is 300t/h with a dimension three ponds for each (650*420*2.2)m³. Active sludge, scum and sludge from waste water treatment plant is dewatered in concentrator and sent to dehydrator by screw pump. By dehydration water content been 84-88% and volume reduced 20 times. Slop oil from all processing units and storing tanks is sent into slop tanks. Other invaluable solid buried in specified location about 12 Kilometer away from the refinery to the east side.
2.7 Classification of Refinery Wastes

Pollution associated with petroleum refining typically includes volatile organic compounds (VOCs), carbon monoxide (CO), sulphur (SO_2), nitrogen oxides (NO_x), particulates, ammonia (NH_3), hydrogen sulphide (H_2S), metals, spent acid and numerous toxic organic compounds, and there are classified as [14]:

A: Wastewater  B: Air Emissions  C: Residuals

2.7.1 Wastewater Types

- **Cooling Water:** As water is cooled in the tower by evaporation, this results in a loss of water in the refinery. Some of the water in the cooling tower is entrained by the large quantities of air passing through the tower and are lost to the atmosphere. Cooling water which normally does not come into contact with oil streams and contains less contaminant than process wastewater. It may contain chemical additives used to prevent scaling and biological growth in heat exchanger pipes.

- **Surface Water Runoff:** Is generated intermittently and may contain constituents from spill to the surface, leaks in equipment and materials in drains.

- **Process Wastewater:** That has been contaminated by direct contact with oil accounts for a significant portion of total refinery wastewater. Many of these are sour water streams and also subjected to treatment to remove hydrogen sulfide and ammonia.

- **Steam losses:** Low pressure steam that is produced in the refinery is vented to atmosphere when it is in excess, other sources include tracing steam that is vented at some locations in the refinery any expected losses should be considered when reviewing the water balance in a refinery.

2.7.2 Air Emissions

The type of air emissions to the environment from refineries is well defined; the main polluting substances are: Sulphur dioxide (SO_2), hydrogen sulfide (H_2S) Oxides of nitrogen (NO_x), Carbon monoxide (CO), Volatile Organic Compounds (VOC), in particular hydrocarbons (excluding methane), Particulate Matter (PM), including metals and their compounds.
Sources of Air Emissions:

- **Combustion Emission**: associated with the burning of fuels in the refinery, including fuels used in the generation of electricity.
- **Equipment Leak Emissions** (fugitive emission): released through leaking valves, pumps, or other process devices. They are primarily composed of volatile compounds such as ammonia, benzene, toluene, propylene, xylene, and other.
- **Wastewater System Emissions**: from tanks, ponds and sewer system drains.
- **Process Vent Emission**: typically include emission generated during the refining process itself. Gas streams from all refinery processes contain varying amounts of refinery fuel gas, hydrogen sulfide and ammonia.
- **Storage Tank Emissions**: released when product is transferred to and from storage tanks.

2.7.3 Residuals Types

- **Non-Hazardous Residuals**: Are incinerated, landfilled or regenerated to provide products that can be sold off-site or returned for re-use at a refinery.
- **Hazardous Wastes**: Are regulated under the Resource Conservation and Recovery Act (RCRA). Listed hazardous waste include oily sludge, slop oil emulsion solids, dissolved air flotation floats, leads tank bottom corrosion solids and waster from the cleaning of heat exchanger bundles.
- **Toxic Chemicals**: Are also use in large quantities by refineries. These are monitored through the Toxic Release Inventory (TRI).

Both hazardous and non-hazardous solid wastes are generated, treated and disposed off.
Treatment of these wastes includes incineration, land treating off-site, land filling on-site, land filling off-site and other treatment methods.[15] Figure (2.4) shows the refining sludge paths.

**Figure (2.4) The Refinery Sludge paths**

*Source: TGM for Petroleum Refining Industry*

At the refinery, proper waste minimization and management is a high priority. The refinery uses a variety of techniques to reduce or recycle waste and transform it into useful products.
2.8 Quantification of Waste Discharges

2.8.1 Air Emissions

Air emissions include point and non-point sources. Point sources re emissions that exit stacks and flares which can be monitored and treated. Non-point sources are fugitive emissions which are difficult to locate and capture.

Fugitive emissions in refineries arise from valves, pumps, tanks, pressure relief valves, flanges, and so on. For example, steam generators are potential sources of SO$_x$, NO$_x$, CO, particulates and hydrocarbons emissions.

Air pollutants produced by refineries are very risky to human health. In addition air pollutants can damage on the ozone layer, water and air. Table 2.1 below shows some of the major air pollutants emitted by refineries.

Table 2.1 Air Pollutants Produced By Oil Refinery

<table>
<thead>
<tr>
<th>Main Air Pollutants</th>
<th>Main Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>Process furnaces, broilers, gas, turbines, fluidized catalytic cracking regenerators, CO broilers, flare systems, and incinerators.</td>
</tr>
<tr>
<td>SO$_x$</td>
<td>Process furnaces, broilers, gas, turbines, fluidized catalytic cracking regenerators, CO broilers, coke calciners, sulpher recovery unit (SRU).</td>
</tr>
<tr>
<td>NO$_x$</td>
<td>Process furnaces, broilers, gas, Turbines, fluidized catalytic cracking regenerators, CO broilers, coke calciners, sulpher recovery unit (SRU)., flare systems, and incinerators.,</td>
</tr>
<tr>
<td>CO</td>
<td>Process furnaces, broilers, gas, turbines, fluidized catalytic cracking regenerators, CO broilers, coke calciners, sulpher recovery unit (SRU)., flare systems, and incinerators.</td>
</tr>
<tr>
<td>Particulates</td>
<td>Process furnaces, broilers, particularly when firing liquid refinery fuels. Fluidized catalytic cracking regenerators, CO broilers, coke plants and incinerators.</td>
</tr>
</tbody>
</table>

Source: TGM for Petroleum Refining Industry
Most refinery process units and equipment are manifolded into a collection unit, called the blowdown system. These blowdown system handle liquid and gas safely. The gaseous component is either discharged directly to the atmosphere or combusted in a flare. The major air emissions from blowdown systems are hydrocarbons in the case of direct discharge to the atmosphere and sulphur oxides when flared.

2.8.2 Wastewater

“Wastewater” means the water discarded and discharged and where “discharged” aspect is stressed. “Sewage” refers to the water polluted by dirty things and where “dirty” aspect is stressed. A considerable quantity of production drainage is not dirty (such as cooling water), so the word “wastewater” is more applicable for all kinds of drainage. When water quality is turbid, both terms can be interchangeable.

(i) Classification of Wastewater

- According the sources of wastewater, it can be classified into domestic, sewage, and industrial wastewater.
- According to chemical category of pollutants, the wastewater can be classified into organic wastewater and inorganic wastewater. The former contains mainly organic pollutants that have biological degradability; the latter contains mainly inorganic pollutants that have no biological degradability.
- According to different toxic substances, wastewater can be classified into phenol-containing wastewater, mercury-containing wastewater, cyanogens-containing wastewater, etc. “Mercury-containing wastewater” means that the major toxic substance contained is mercury, but which does not mean that mercury content is the highest, or mercury is the only pollutant.
2.9 Treatment Technologies for Petroleum Refinery Effluents

The different technologies used for the treatment of petroleum refinery effluents (PRE). Broadly, PRE treatment is accomplished in two stages, namely, a series of pre-treatment steps, in which wastewater contaminants are decreased to certain acceptable discharge limits.

Most researches are focused on treating singular contaminants found in PRE, e.g., phenols, sulphides, oil, grease and other organic components. This review focused on works that investigated PRE treatment by monitoring general refinery wastewater parameters, namely, chemical oxygen demand (COD), biological oxygen demand (BOD), total petroleum hydrocarbon (TPH), oil and grease (O&G), sulphate and phenols at advanced treatment steps [16].

There are two basic treatment stages. The first stage consists of mechanical and physicochemical treatment followed by the advanced treatment of the pre-treated primary effluent.

Figure (2.5) is atypical waste treatment arrangement.
(i) Pre-treatment step

The primary treatment step is essential as it allows for the efficient and prolonged use of the secondary treatment unit.

Here the heterogeneous component of the effluent i.e., suspended solids (SS), immiscible liquids, solids particles and suspended substances (colloids or dispersions) are reduced significantly.
This is achieved mechanically by gravity in API separators or separation tanks.

Without the primary treatment the presence of salts and sulphide in excess of 20 mg/L can strongly inhibit subsequent biological operation. [16]

Colloids and dispersion also hinder or damage equipment during the preceding stage.

The mechanical step is followed by the physiochemical step, in which heavy metal concentration is decreased and small sized suspended solids are further reduced by agglomeration into large-sized particles to easy removal by filtration, sedimentation or flotation. [16]

Figure (2.6) is shows the objectives of each treating process.

**TREATMENT CHAIN**

- **Oil – water separation**
- **Equalization**
- **Coagulation / Flocculation**
- **Dissolved Air Floatation**
- **Biological / Adsorption**

**OBJECTIVES**

- Separate oil from water
- Decrease organic load and salt
- Shock
- Remove turbidity and organic load abatment
- Remove suspended organic solid
- Remove mineralize organic pollutant

*Figure(2.6) Schematic diagram of sequence for treating petroleum refinery effluent*
(ii) Secondary treatment

Objective is the decomposition of dissolved organic matter by means of using biologically active sludge.

**Secondary treatment**: Biochemical treatment is called secondary treatment. The objects of secondary treatment are bodied or dissolved organic substances. The employed facilities include biological aerated filter and secondary sedimentation tank.

Consist of the biological treatment of the effluent from primary treatment to remove the residual organics, suspended, colloidal and dissolved solids.

Three approaches are used to accomplish secondary treatment

(i) **Fixed film systems**: Microorganisms grow on substrates (rocks, plastic, sand) over which the wastewater is spread over. The film of microorganisms grows and thickens while the nutrients are absorbed. Some examples are rotating biological contactors (RBC), trickling filters and sand filters.

(ii) **Suspended film systems**: Microorganisms are suspended in wastewater and once they absorb nutrients, reproduce and then are settled out as sludge. A portion of the sludge is pumped back into the incoming wastewater as “seed” microorganisms while the other part is sent to sludge treatment. Examples of such systems are extended aeration, activated sludge, sequential batch reactor systems and oxidation ditch.

(iii) **Lagoon systems**: Are shallow ponds designed to hold wastewater for several months while is treated through a combination of physical, biological and chemical processes. Some aeration devices can be added to rise the system efficiency. The most common types of lagoons are:

A: - Anaerobic lagoons.

B: - Naturally aerobic lagoons.
(iii) Advanced treatment

Is Any process applied after secondary treatment designed to produce an effluent of higher quality to protect the receiving water or to provide reusable water for its further domestic and/or industrial recycling (cooling water supplies).

The objective of this stage is to reduce the effluent contamination level to allowable limits for discharge into water bodies. Several techniques that are used as advance treatment method are now briefly discussed.

Although biological systems are capable of removing many of the dissolved organic carbons, recalcitrant components are not adequately eliminated. Petroleum effluents contain a higher number of refractory compounds therefore completely degrading them through biological means prove difficult. This is supported by higher COD values observed in some treat effluents [17]. The remaining COD of treated effluents reflects the non-biodegradable components [18]. To enhance biodegradability, bacterial activity is increased through immobilization on an inert support in fixed bed reactor.
2.10 EFLUENT TREATMENT METHODS

Effluent can be treated in a number of different ways depending on the level of treatment required. These levels are known as preliminary, primary, secondary and tertiary (advanced).

The mechanism for treatment can be divided into three broad categories: physical, chemical, and biological, which all include a number of different processes (table). Many of these processes will be used together in a single treatment plant.

**Table 2.2 waste water treatment levels and process**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Description</th>
<th>Processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preliminary</td>
<td>Removal of large solids and greases</td>
<td>Physical</td>
</tr>
<tr>
<td>Primary</td>
<td>Removal of floating and settleable materials such as suspension solids and organic matters</td>
<td>Physical and chemical</td>
</tr>
<tr>
<td>Secondary</td>
<td>Removal of biodegradable organic matter and suspended solid</td>
<td>Physical and chemical</td>
</tr>
<tr>
<td>Tertiary</td>
<td>Removal of residual suspended solids / dissolved solids</td>
<td>Physical, chemical and biological</td>
</tr>
</tbody>
</table>

Chemical, physical, and biological methods have been used to remove the organic compounds from the waste water, and biological method has been paid much attention owing to its economics and ecologic superiority.

The biological treatment method is easy to apply and with improvement the effluent quality and leads to clean production and clean technology.

The biodegradation rate and biodegradation degree of the organic substance partly depended on the characters of the substance.

Some of the organic pollutant like organic matters, organophosphorus pesticide which have relatively high water solubility and low acute toxicity are bio available and easy to be degraded.
2.10.1 Physical Treatment

Physical treatment or physical unit operations usually includes following treatment techniques: screening, equalization, cooling, sedimentation and filtration.[19]

Common physical unit operation include among other Processes screening, flow equalization, sedimentation, clarification and aeration.

(i) Screening

A screen openings of uniform size is used to remove large solid such as plastics, cloth, polythene etc which may damage process equipment, reduce the effectiveness of the contaminate waterways.

(ii) Flow Equalization

The objective of the equalization system is to minimize the fluctuation caused due to either sudden of flow or composition in the wastewater treatment plant.

Flow equalization: Flow equalization provides dampening of the flow variations, thereby reducing potential spikes in flow and loads to the downstream units; it also reduces the size of the downstream units and cost of the overall refinery wastewater system.

Concentration equalization: This system provides dampening of contaminants, thereby preventing the shock loading of the downstream units such as biological systems. In a biologically-based system, performance is limited by the capacity of the microorganisms to adapt to changing conditions of variation in flow and composition.

(iii) Sedimentation and Filtration

The flocs formed in flocculation are large enough to be removed by gravitational settling, also known as sedimentation. This is achieved in a tank referred to as the sedimentation tank, settling tank or clarifier. Sedimentation is also used to remove grit and suspended solid, to produce clarifier effluent, and to thicken the sludge produced in biological treatment. Flocculation and sedimentation should remove most of the suspended solids and apportion of the BOD.
(iv) Aeration

Aeration is required in biological treatment processes to provide oxygen to the microorganisms that breakdown the organic waste. Two main methods are used for this, either mechanical agitation of the water so that air from the atmosphere enters the water, or by introducing air into the tank through diffusers.

2.10.2 Chemical Treatment

Chemical treatment or chemical unit processes usually includes following treatment processes and techniques: neutralization, coagulation, and flocculation, chemical precipitation, oxidation, reduction, ion – exchange, chemical adsorption, reverse osmosis and electro – dialysis.

Chemical unit processes are always used with physical operation and may also be used with biological treatment processes, although it is possible to have purely physicochemical plant with no biological treatment.

(i) pH Control

Microorganism prefers to survive in neutral or acid environment with suitable pH range at 6-9.

The best pH to sustain the growth of nitrifying bacteria is about 7.0 higher or lower pH will spoil activated sludge and degrade the effect of treatment sharply.

(ii) Chemical Precipitation

Chemical precipitation is the most common method for removing dissolved metals from a wastewater solution containing toxic metals to convert the dissolved metals into solid particle form a precipitation reagent is added to mixture.

A chemical reaction, triggered by the reagent, causes the dissolved metals to form solid particles. Filtration can then be used to remove particles from the mixture.

In hydroxide precipitation a commonly used chemical precipitation process, calcium hydroxide is used as reagent to create solid metal hydroxides.
However it can be difficult to create hydroxide from dissolved metal particles in wastewater because many wastewater solutions contain mixed metals [20].

Certain processes such as reactive dyeing require large quantities of alkali but pretreatment and some washes can be acidic.

It is therefore necessary to adjust the pH in the treatment process to make the wastewater pH neutral.

This is particularly important if biological treatment is being used as the microorganism used in biological treatment require pH in the range of 6-8 and will be killed by highly acidic or alkali wastewater various chemicals are used for pH control.

(iii) Chemical Coagulation and Flocculation

Coagulation is a complex process but generally refers to collecting into larger mass the minute solid particles dispersed in a liquid.

Chemical coagulation such as aluminium sulphate (alum) or ferric sulphate may be added to wastewater to improve the attraction of fine particles called flocs.

A chemical flocculent usually a polyelectrolyte enhances the flocculation process by bringing together particles to form larger flocs, which settle out more quickly. Flocculation is aided by gentle mixing which causes the particles to collide.

Coagulant dose is a key of process – control factors because of different water quality conditions can have an effect on different dose of coagulant.

It was found that coagulant doses are controlled by dissolved organic carbon (DOC) concentration rather by turbidity in most surface waters.

These makes an adjustment on coagulant dosage is important to ensure the effectiveness for maintaining settled raw water quality in plants.

Coagulation – flocculation consists on the addition on the clarification tanks of chemical products that accelerate the sedimentation (coagulants).
The coagulants are inorganic or organic compounds such as, Aluminium sulphate, Aluminium Hydroxide Chloride or high molecular weight cationic polymer.

The purpose of the addition of coagulant is to remove almost 90% of the suspended solids from the wastewater at this stage in the treatment process.

(iv) Dissolved Air Flotation

Dissolved air flotation (DAF) is a water treatment process that clarifies wastewaters by the removal of suspended matter such as oil or solids.

The removal is achieved by dissolving air in the wastewater under pressure and then releasing the air at atmospheric pressure in a flotation tank or basin.

The released air forms tiny bubbles which adhere to the suspended matter causing the suspended matter to float to the surface of the water where it may then removed by a skimming device.

Dissolved air flotation is widely used in treating the industrial wastewater effluents from oil refiners, petrochemical and chemical plants, natural gas processing plants, paper mills, general water treatment and similar industrial facilities.

A very similar process known as induced gas flotation is also used for wastewater treatment.

Froth flotation is commonly used in the processing of minerals.

In the oil industry, dissolved gas flotation (DGF) units do not use air as the flotation medium due to the explosion risk. Natural gas is used instead of to create the bubble

2.10.3 Biochemical Unit Processes

Biochemical treatment is an important and integral part of any wastewater treatment plant that treats wastewater from either municipality or industry having soluble organic impurities or a mix of the two types of wastewater.

The objective of biological treatment of industrial wastewater is to remove or reduce the concentration of organic and inorganic compound.
Biological treatment process can take many forms, but all are based around microorganism mainly bacteria.

These microorganism use components of the effluent as their ‘food” and in doing so break them down to less complex and less hazardous compounds.

In the process the microorganism increase in number there are two main types of processes these involve suspended microbial growth (eg activated sludge ) and attached microbial growth (eg fixed film ) .

With both approaches large population of microorganism are brought into contact with effluent in the presence of an excess of oxygen in both systems the microbial population has to be retained in a tank referred to as the reactor.

With suspended growth systems microbes in small aggregates or “flocs” (this is known as activated sludge)

**Activated Sludge (AS)**

The activated sludge process is used to treat waste stream that are high in organic loading and biodegradable compounds. it is most widely used biological process for the treatment of edible oil refinery wastewater

In the traditional percolating filters effluents is sprayed over the medium and trickles through a packed bed with oxygen entering from the air in more recent reactor designs the medium (usually plastic ) is submerged in effluent and air is blown into the base of reactor .

Submerged fixed film reactors using plastic media require much less land.

Fixed film systems require a final clarifier to remove particles of biofilm that become detached from the medium .however this material is not recycled to the reactor. while most of the activated sludge is recycled some may be surplus to requirements and needs to be disposed of appropriately so that the pollutant now present in this sludge do not enter the water cycle .

The treated liquid is discharged to the environment or taken for further treatment depending on the desired standard of effluent quality or the required use of wastewater.
Biological treatment plants must be carefully managed as they use live microorganisms to digest the pollutants. For example some of the compounds in the wastewater may be toxic to bacteria used and pre-treatment with physical operations or chemical processes may be necessary. It is also important to monitor and control pH as adverse pH may result in death of the microorganisms. The ETP must be properly aerated and must be operated 24 hours a day, 365 days a year to ensure that the bacteria are provided with sufficient “food” (i.e. wastewater) and oxygen to keep them alive. Like humans, microorganisms need a “balanced diet” with sources of carbon, nitrogen, phosphorus and sulphur. It is possible to replace these nutrients by substituting the liquid portion of effluent from toilets, which rich in nitrogen and phosphorus containing chemicals (the solid portion may cause problems).

(i) Aerobic and Anaerobic

Aerobic means in the presence of air (oxygen) ; while anaerobic means in the absence of air (oxygen). These two terms are directly related to type of bacteria or microorganisms that are involved in the degradation of organic impurities in a given wastewater and the operating conditions of the bioreactor.

Aerobic treatment processes take place in the presence of air and utilize those microorganisms (also called aerobes) , which use molecular/free oxygen to assimilate organic impurities i.e. convert them in the to carbon dioxide, water and biomass.

The anaerobic treatment processes, on other hand take place in the absence of air (and thus molecular/free oxygen) by those microorganisms (also called anaerobes) which do not require air (molecular/free oxygen) to assimilate organic impurities. The final products of organic assimilation in anaerobic treatment are methane and carbon dioxide gas and biomass.

Major Differences in Aerobic and Anaerobic Treatment

Aerobic Treatment

- Process principle: Microbial reactions take place in the presence of molecular/free oxygen, Reactions products are carbon dioxide, water and excess biomass.
• **Applications:** Wastewater with low to medium organic impurities (COD<1000ppm) and for wastewater that are difficult to biodegrade e.g. municipal sewage, refinery wastewater etc. Net Sludge Yield: Relatively high.

• **Post Treatment:** Typically direct discharge or filtration/disinfection

• **Example Technologies:** Activated Sludge e.g. Extended Aeration, oxidation Ditch, Fixed film processes e.g. Trickling filter.

**Anaerobic Treatment**

• **Process principle:** Microbial reactions take place in the absence of molecular/free oxygen, Reactions products are carbon dioxide, methane and excess biomass.

• **Applications:** Wastewater with medium to high organic impurities (COD>1000ppm) and easily biodegradable wastewater e.g. food and beverage wastewater rich starch/sugar/alcohol. Net Sludge Yield: Relatively low.

• **Post Treatment:** Invariably followed by aerobic treatment

• **Example Technologies:** Continuously stirred tank reactor/diester

It is not anaerobic or aerobic treatment, but a combination of the two types of the technologies that give an optimum configuration for those wastewater treatment application where the organic impurities are at a relatively higher concentration.
2.11 Sludge Treatment

To guarantee proper sludge thickness in CASS pond, the sludge pump set at the end of CASS pond will deliver the surplus sludge into sludge machine for de-watering, the filtering water will be lead to water collection pond for treatment. The dried sludge cake will be transported out for filling land.

Character and Index of whole System:
This system will set two separate CASS ponds, i.e. System 1(A) and System 2(B), both of them can work separately in manual operation and automatic operation and form a system by itself. There is no relationship between the two ponds, but should decide a right and proper intermediate time of the two ponds in order to make the water in wastewater collection & adjustment pond can be discharged evenly.

This system had following character:

a. Small land area, but needed primary sedimentation pond and a second sedimentation pond and complicated water recycling system

b. Few mechanical equipment, low investment and low running costs.

c. Simple operation, high automatic level.

d. Can amortize the fluctuation of water quality by adjusting aeration time.

*Table (2.3): The performance index of this system is as following*

<table>
<thead>
<tr>
<th>NO</th>
<th>Item</th>
<th>Inlet Water</th>
<th>Outlet Water</th>
<th>Removing Rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Water Quantity</td>
<td>1800 t/d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>COD</td>
<td>450 mg/l</td>
<td>100 mg/l</td>
<td>77.8</td>
</tr>
<tr>
<td>3</td>
<td>BOD₅</td>
<td>300 mg/l</td>
<td>20 mg/l</td>
<td>93.3</td>
</tr>
<tr>
<td>4</td>
<td>SS</td>
<td>200 mg/l</td>
<td>5 mg/l</td>
<td>97.5</td>
</tr>
<tr>
<td>5</td>
<td>Oil and Grease</td>
<td>50-100 mg/l</td>
<td>&lt; 3 mg/l</td>
<td>97</td>
</tr>
<tr>
<td>6</td>
<td>pH</td>
<td>6-9</td>
<td>6-9</td>
<td></td>
</tr>
</tbody>
</table>
2.12 Oily Waste Water Treatment Units:

(i) Design Basis in KRC:
Anoxic-aerobic (A/O) treatment process is adopted to eliminate ammonia nitrogen and total nitrogen from water and ensure the quality of drained water after treatment to reach the national standard of emission. The inlet COD should be less than 800mg/L and ammonia concentration should be lower than 50 mg/L. The designed treatment capacity is 300 tons/h, the remained activated sludge and waste oil from oil separator would be sent into dry machine and process unit respectively.

The anoxic biochemical technique uses contact oxidation method (biological membrane method) which is endurable to shock load and strong in adapting to environment, in addition with less generation of sludge. The adoption of two-stage air flotation technique has reinforced the capability of oil removal and improved the effect of removing waste oil.

Chain-type oil and sludge skimmer and chain-type slag skimmer are used. A regulating tank of large capacity is set up to regulate the shock volume and quality of water.

Chemical, alkaline and acid are injected through measuring pumps. The dosages are relative constant and would be adjusted according to the process condition.

In order to monitor the inlet/outlet water quality and process water quality situation, some analysis items have to be analyzed such as online pH and DO analyzers. The other analysis items would be done by central lab according to the regulated analysis frequency such as COD, BOD ammonia SS, oil content, phenol etc. [21]
2.13 Sour Water Treatment

Sour water is generally classified as phenolic or non-phenolic. Non-phenolic water contains almost exclusively NH₃, H₂S and possibly a trace of CO₂. It is generated by refinery hydro treating (hydrodesulphurization, or HDS) unit. When stripped of contaminants, non-phenolic water can typically be recycled for reuse in the HDS unit as wash water, or it can be used as make-up water to the crude desalting process. Phenolic (or more broadly, non-HDS) water typically contains H₂S, phenols and caustic.

The 1.0 million t/y sour water stripping unit of Khartoum Refinery Co Ltd is configured to be single-column low pressure stripping process. The feedstock for the unit is the sour water coming from such units as Residual Fluid Catalytic Cracking Unit (RFCC), Delayed Coking Unit (DCU), Coker Gasoline/diesel Hydro Treating Unit (GDHT) as well as Diesel Hydroforming (DHT) etc. Design processing capacity of the unit is 1.0 million t/y. The unit consists of these sour water pretreatment system, sour water stripping system (SWS), sour gas incinerator system (SGI), waste gas sweetening facility system (WGS), condensate water recovery system (CWR). Design processing capacity for sour water pretreatment and sour water stripping systems is 125 t/h. Normal processing capacity for sour gas incinerator is 2.401 t/h, and the maximum is 2.40 t/h. Design capacity for condensate water treatment system is 50 t/h with on stream hours of 8000 h per annum and operating flexibility of 60~110%. Processing capacity for waste gas treatment facility is 100~300 m³/h, the maximum is 600 m³/h selecting DCS for control.

2.13.1 Design Basis of the Sour Water Unit

1. Degassing Section:
The sour water is received from the refinery in the flash drum, where light hydrocarbons are flashed off.

2. De-Oiling Section:
(Tank in tank) regulating tank (WS-11) type is a separator tank which integrates centrifuge. The equipment promote three phase separation for oily water light oil float to the upper of separation
chamber, and sent to external slop collection tank. The deposited solid phase substance (oily sludge) can be water pressurized and then discharged manually from cone of the unit.

3- **Stripping Section:**

The sour water is then heated in the feed/bottoms exchanger and fed to the stripper column. Steam, generated in the reboiler, heats the water and strips the hydrogen sulfide (H₂S) and ammonia (NH₃) from the water. The stripped water from the column is cooled in the feed/bottoms exchanger and in the stripped water cooler, and returned to the refinery. The (H₂S) and (NH₃) removed from the sour water is cooled in the pump-around cooler system or in an overhead condenser system and sent to the sulfur recovery unit for further processing. Caustic soda injected in the column to control the PH for more efficient separation.

4- **Condensate Water Recovery Unit:**

To recovery condensate, then much part of the energy consumption for boiler feed water treatment is saved.

5- **Incineration section:**

Sour gas incinerator uses hot incineration to get sour gas burnt at 1350 -1400°C till discharged to the atmosphere by stack:

\[ \text{H}_2\text{S} + \frac{3}{2} \text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O} \]
\[ 2\text{NH}_3 + \frac{3}{2} \text{O}_2 \rightarrow 3\text{H}_2\text{O} + \text{N}_2 \]
2.14 Oxidation Ponds

The three Oxidation Ponds in Khartoum refinery situated at three decreasing levels. During construction, plastic layer had been installed at the bottom and the sides of the ponds to prevent water seepage. The area of the ponds is 0.78 km$^2$. The flow is evenly distributed to preserve a 1.2m water level. Meteorological experiments of the area, estimated the evaporation rate to be 17.1mm/day [22]

The Oxidation Ponds at Khartoum Refinery are the final disposal terminals of treated wastewater effluent discharged from the treatment plant. The ponds are about 1100m in length and 625m wide.

The effluent is odorless and greenish in color. No traces of oil (i.e. oil films) could be seen.

The total area of the ponds is about 687500m$^2$.

A level of 1.2m is always maintained through even distribution of wastewater effluent into the ponds, using control valves. There are embankments 3m wide around the three ponds,
Plate (2.8): Oxidation pond Khartoum Refinery
CHAPTER THREE
Materials and Methods

3.1 Introduction
The wastewater treatment unit of Sudan Khartoum Oil Refinery was designed by China petroleum & Chemical Corporation Luoyang Design Institute in 1998 and put into production in October 1999 after its construction had been completed by China petroleum No.1 Engineering Company. The designed capacity of the unit is 300 m$^3$/h, including alkaline containing sewage 40 m$^3$/h and sulfur containing sewage 37 m$^3$/h. The sewage after treatment is delivered to the oxidation pond outside the plant. Capacity of oxidation pond: 1260*650*0.5m, the designed rate of evaporation: 17.1mm/d.

The oily wastewater is pumped into oil separator where the most of floating oil will be separated from water by gravity effect. Then it flows into two stages Dissolved Air Floatation pond (DAF) to eliminate remaining emulsified oil. Afterwards, it moves into biochemical reaction ponds where most of organic pollutants such as BOD$_5$/ COD are biodegraded. And through nitrification and de-nitrification effects, a part of ammonia is turned into nitrogen to atmosphere. Finally, it enters sedimentation ponds where water and activated sludge are separated. The oily slurry from oil separator, dissolved air flotation ponds and remained activated sludge from biological reaction system is dewatered by centrifuge dry machine. The waste oil from this plant is recovered by DCU unit. The treated waste water into oxidation ponds. The water in oxidation ponds is vaporized into atmosphere.

The KHARTOM REFINERY Wastewater contains several pollutants including variable concentration of oil, phenols, suspended solids, sulfides, oxygen demand, bearing material and other harmful contaminants.

3.2 The Materials:
Materials used during this research work are taken from K.R.C waste water treatment system and they may be categorized as follows:

a. Sewage water.

b. Waste water.
c. Mixture of sewage and waste water.

d. Chemicals for the necessary tests.

All the tools and hardware required for the tests have been mentioned in the methods. All the test methods and procedures are of the KRC manual [21]

3.3 Test Methods:

A test method is a method for a test in science or engineering, such as a physical test, chemical test, or statistical test. It is a definitive procedure that produces a test result.

A test can be considered a technical operation or procedure that consists of determination of one or more characteristics of a given product, process or service according to a specified procedure. Often a test is part of an experiment.

The test result can be qualitative (yes/no), categorical, or quantitative (a measured value). It can be a personal observation or the output of a precision measuring instrument.

Usually the test result is the dependent variable, the measured response based on the particular conditions of the test or the level of the independent variable.

Some tests, however, may involve changing the independent variable to determine the level at which a certain response occurs: in this case, the test result is the independent variable.

3.3.1 Test Method for Ammonia Nitrogen

Narsh colorimetric method or phenol ate method can be used for testing the ammonia nitrogen in water. Phenolate method is more sensitive than Narsh method. The ammonia nitrogen in water is not particularly stable, besides adding proper conservant and transport under a cooling condition; the test must be done within the shortest time.

(i) Principle:

Under alkali condition, ammonia in water and Narsh reagent (K₂HgI₄) react to produce compound (NH₂Hg₂OI), which is yellow to brown. The color and the content of ammonia nitrogen are in direct proportion.

(ii) Instrument:

a. 500ml glass distillatory flask
b. 50ml color comparison tube
c. spectrophotometer
(iii) Steps of the Tests:

- **pre-treatment of water sample**
  The colorless and clear water sample can be tested directly. The water sample with high color, turbidity and disturbing substance need be distillated or depositing of mixing-condensing.

- **distillation**

- **coagulation and sedimentation**
  To 200ml of water sample 2ml zinc sulfate solution are add , and blended uniformly. 0.8-1ml sodium hydroxide solution are add to make the pH value 10.5, this is held for several minutes, and then the clear liquid is tested for color comparison. The water sample deposited through zinc sulfate and sodium hydroxide. The water sample is normally clarified.
  
(iv) Test:

  a. Take 50ml clarified water sample or pre-heated water sample (if ammonia nitrogen content is more than 0.1mg, get proper amount of water sample and add pure water to 50ml ) from 50ml color comparison tube.

  b. In 10 color comparison tubes of capacity of 50ml, the following quantities of ammonia nitrogen solution: 0, 0.10, 0.30, 0.50, 0.70, 1.00, 5.00, 7.00, 10.00 are taken and pure water is used to dilute samples to 50ml.

  c. Respectively add 1ml of potassium sodium tartrate solution into the water sample tube and standard solution tube. Blend uniformly, add 1.0ml of Narsh reagent, blend uniformly, keep still for 10minutes, put under the wavelength of 420nm, use 1cm color comparison vessel, take pure water as referring comparison, and test the light absorption degree. If the ammonia nitrogen content is less than 30μm, use a 3cm color comparison vessel. If the ammonia nitrogen content is less than 10μm, test by eyes.

  d. Draw the standard curve, check the ammonia nitrogen content from the curve, or check it from the eye test records.
(v) **Calculations:**

The ammonia concentration (N) in water sample is calculated by the following equation:

\[ C = \frac{W}{V} \] \hspace{1cm} \text{(3.1)}

Where:
- C: The ammonia concentration (N) in water sample, mg/L
- W: Ammonia nitrogen content got from the standard curve, μm,
- V: Volume of the water sample, ml.

### 3.3.2 Test method for pH value (pH potential method):

(i) **Scope:**

a. This method is suitable for testing pH value of the drinking water and the water from the water source.

b. The following factors won’t disturb the test: water color, turbidity, free Cl, oxidant, reducer, high salt content. But, in the stronger alkali solution, when there is large quantity of Sodium ion, there will be difference and cause low readings.

c. Use this method to test pH, it can précised to 0.01pH unit.

(ii) **Principles:**

Take the glass potentiometer as the indicating electrode, saturate Hg electrode as the reference electrode, insert into the solution to structure battery. At 25°C, each unit pH scale is equivalent to 59.1mV electromotive force. Read pH value reading directly at the instrument.

(iii) **Instruments:**

Precision acidimeter

a. The following standard buffer solutions are all need prepared by the pure water which is boiled and cooled down. Store the ready solution in a polypropylene bottle or hard glass bottle. This kind of solution can be stable for 1 to 2 months.
b. pH standard buffer solution A: get 10.21g of \( \text{KH}_2\text{C}_8\text{H}_4\text{O}_4 \), which is dried for 2 hours at 105 °C, dissolve it with pure water and dilute to 1000ml. The pH value of this solution is 4.00 at 20°C.

c. pH standard buffer solution B: get 3.40g of \( \text{KH}_2\text{PO}_4 \) and 3.55g \( \text{Na}_2\text{HPO}_4 \), which are dried for 2 hours at 105 °C, dissolve it with pure water and dilute to 1000 ml. The pH value of this solution is 6.88 at 20°C.

d. pH standard buffer solution C: get 3.81g of \( \text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O} \), which is dried for 2 hours at 105 °C, dissolve it with pure water and dilute to 1000 ml. The pH value of this solution is 9.22 at 20°C.

(iv) Procedure:

a. Before using, the glass electrode shall be dipped in pure water for 24 hours.

b. Use pH standard buffer solution A, C to test instrument and electrode which must be normal.

c. When testing, use the standard buffer solution with pH value which is close to the water sample to calibrate scale.

d. Use washing bottle with pure water to spray slowly the two electrodes for several times, and then use water to spray them 6-8 times, and then put into water sample. One minute later, read pH value directly from the instrument.

3.3.3 Test methods for Chemical Oxygen Demand:
The instrument can test directly the sample of COD less than 1000 ppm. The sample of COD more than 1000 ppm can be diluted before test.

(i) Principle:
COD test method is based on Coulomb titration of constant current, its principle follows Coulomb’s law.

(ii) Reagents:
Distilled water is used in reagent preparation and analysis.

a. Distilled water

b. 1/120 mol/l \( \text{K}_2\text{Cr}_2\text{O}_7 \) solution
c. Sulfuric acid -- Silver sulfate reagent. Dissolve silver sulfate of 6.0g into concentrated sulfuric acid.

d. Ferrite sulfate solution of 0.5mol/l. Dissolve ferric sulfate of 200g into the distilled water of 1liter. If it’s difficult to dissolve, put it on an electric stove for heating and agitating till it is dissolved.

e. Saturated potassium sulfate solution 6.3M sulfuric acid solution

(iii) Instruments:

f. Chemical oxygen consumption instrument.

g. Counteraction cup: 100ml.

(iv) Procedure:

Put potassium dichromate 1/120 mol of 3.0ml into counteraction cup, add proper amount of water sample (the maximum volume not exceed 10.0ml according to the pollution extent), then add sulfuric acid—silver sulfate reagent of 17.0ml for heating and recycling of 15 minutes. After cooling, add 33.0ml distilled water and 0.5M of 7ml ferric sulfate solution, cool it to the ambient temperature for test. Take distilled water of 10.0ml to make blank test in the same way (if test value of blank sample is less than 102mg/l, the blank sample can’t be used).

3.3.4 Test methods for Sulfide:

(i) Principle:

Sulfide reacts with zinc acetate to produce settling of white zinc sulfide dissolve this settling in acid, and let it react with standard iodine, then use sodium hyposulfite to titrate the excessive amount of iodine.

(ii) Instruments:

a. Acid burette

b. Iodine flask

c. Vacuum pump, Buckner filter

d. Middle-speed quantitative filter paper
(iii) Reagents:

a. 1% fecula indicator

Weigh 10.0g of soluble fecula and blend into pasty state with small amount of water, then add boiling distilled water to 1000ml, after cooling, add 1.25g of salicylic acid to prevent metamorphosing.

b. 1.5 sulfuric acid solution.

c. 1mol/l sodium hydroxide (NaOH).

Weigh 40.0g of sodium hydroxide and dissolve it into water of 500ml, cool them to ambient temperature, and then transfer into a volumetric flask of 1000ml, dilute to graduation and shake to a uniform state.

d. 10% zinc acetate solution

Weigh 100.00mg of zinc acetate and dissolve it into water, add 10ml of concentrated hydrochloric acid and dilute to 1000ml.

e. 0.05mol/l sodium hyposulfite (Na$_2$S$_2$O$_3$.5H$_2$O)

Weigh 12.4g of sodium hyposulfite and 0.4g of sodium hydroxide, dissolve them in distilled water which has been boiled and cooled, and dilute with the same distilled water to 1000ml. Store in a brown bottle for standardizing with standard potassium dichromate solution or iodine water.

f. 1/120 mol/l potassium dichromate (K$_2$Cr$_2$O$_7$)

Weigh 2.4516g (1.2258g) of potassium dichromate which has been dried in a 105 oven for 2 hours and cooled, and dissolve it in water, transfer into a volumetric flask of 1000ml (500ml), dilute to graduation.

g. Standardization of 0.05mol/l sodium hyposulfite:

Take an iodine flask of 250ml; add about 1g of potassium iodide into it, pour 50ml of distilled water for dissolution, accurately add 10.0ml of 1/120mol/l potassium dichromate standard solution and 5.0ml of 3mol/l sulfuric acid solution, settle for 5 minutes, then titrate with sodium hyposulfite solution to light yellow, add 1ml of 1% fecula indicator and continue to titrate till blue just disappears, record consumed quantity(note: at end point, solution should indicate light green of complex ion with three valency, otherwise...
increase sample quantity or concentration of standard solution), adjust the concentration of sodium hyposulfite to 0.05mol/l.

h. 0.05mol/l standard iodine water

Weigh 6.35g of iodine and put into potassium iodide solution prepared before (20g of potassium iodide into 20ml of distilled water). When iodine is dissolved completely, transfer the solution into a volumetric flask of 1000ml, dilute with water to graduation.

Take iodine water of 20.0ml into an iodine flask of 250ml, add 50ml of distilled water, 5.0ml of sulfuric acid, titrate with standard sodium hyposulfite solution of 0.05mol/l to light yellow, add 1ml of 1% fecula indicator and continue titrating till blue disappears completely, record the consumption V(ml) of sodium hyposulfite.

Adjust standard concentration of iodine water to 0.05mol/l according to the following formula:

\[ C = \frac{0.05 \times V}{20} \]  

(iv) Procedure:

i. Pour 10ml of 10% zinc acetate solution and 5ml of 1mol/l sodium hydroxide solution into a sample-taking bottle of 250ml, take about 250ml of water sample into this bottle to determine sulfide of water sample.

j. Take 100ml of water sample with immobile liquid, use middle-speed filter paper and vacuum pump to filter white settling, and wash the sediment with distilled water. Put settling and filter paper into an iodine flask of 250ml, add 50ml of distilled water. Agitate and break up filter paper sufficiently, then add 5.0ml of sulfuric acid solution as well as 10.0ml of 0.05mol/l iodine water, cover with a bottle block immediately and seal with distilled water, settle in a dark place for 5.0 minutes, Titrate with 0.05mol/l sodium hyposulfite to light yellow, add 1ml of 1% fecula indicator, continue titrating till blue disappears completely, record consumption V2 (ml) of sodium hyposulfite. Make a blank test in the same way.
(v) Results and Calculation:
Sulfide content in mg of 1 liter of water can be calculated as follows:

\[
S^{2}(mg/l) = \frac{(V_1 - V_2) \times C \times 16 \times 1000}{V} \quad \text{…………………(3.3)}
\]

Where:
- \(V_1\): volume of sodium hyposulfite standard solution for blank test, in ml.
- \(V_2\): volume of sodium hyposulfite for titrating water sample, in ml.
- \(V\): volume of water sample, in ml.
- 16: mole number

Note: In order to prevent the volatilization of hydrogen Sulfide, immobile liquid (10.0ml of 10% zinc acetate solution, 5.0ml of 1mol/l sodium hydroxide solution are used to fix sulfide in water of 250ml) must be added into the sample-taking bottle before sample-taking.

3.3.5 Test methods for Oil content:

This method is used for testing micro oil content of industrial circulation cooling water containing oil content of 0-10mg/L.

(i) Principle:
Aromaticity of industrial circulation cooling water has characteristic absorbency in UV area. Oil content can be tested by testing aromaticity content. To extract Oil of industrial circulation cooling water by petroleum ether (60-90%) as solvent, oil content is determined by measurement of the absorbance at 225 nm.

(ii) Reagents:
- sulfuric acid solution
- petroleum ether: 30-60, 60-90
- sodium sulfate (without water)
- stoma silica gel: 80-100 mesh (or 13x molecular sieve)
- sulfate acid, formaldehyde reagent
(iii) **Instruments:**
- ultraviolet spectrophotometer
- separating funnel: 500ml
- funnel: diameter is 60mm
- measuring flash: 5.ml

(iv) **Analysis steps:**
To draw standard curve

**a.** Precisely get 100mg standard oil sample, which is transferred into a 100ml measuring flash (60-90%), and dilute to the graduation. Get 1ml of standard oil sample containing 1mg, then dilute fivefold, get 1ml of standard oil sample with 0.2mg.

**b.** Respectively 1ml of standard oil samples with 0.2mg, put it into 1, 2,4,6,8, 10ml measuring flasks with capacity of 50ml, use petroleum ether to dilute to the graduation, shake it to be uniform.

**c.** At 225 nm, use 1cm quartz color comparison vessel, take petroleum ether as blank sample, and test the absorbency.

**d.** Take absorbency as y-axis, mg number of oil as the x-axis, draw the standard curve.

**e.** test of water sample:
Take 150-200ml water sample and put it into a separating funnel, add 5ml sulfuric acid solution
add 20ml of petroleum ether, clean the sampling bottles, measuring cylinders, then pour into the separating funnel, violently shake 2-3minutes, and continuously start up piston to discharge gas, keep still for 2-3minutes, separate layers, put the bottom layer water sample into the original sampling bottle.
Put anhydrous sodium sulfate into a funnel with filtering paper to 1/3 height, suck out the filtered object from the petroleum ether and filter it into a 50ml measuring flask.
Transfer the water sample into the separating funnel again, repeat 4.2.2 and 4.2.3, then put 10ml of petroleum ether to clean the funnel and filtering bottle. Collect the extracting
liquid of petroleum ether into one measuring bottle, use petroleum ether to dilute it to the
graduation, shake it to be uniform

(v) Calculations:
Calculate the oil content X(mg/L) in the water sample as the follows:

\[ X = \left( \frac{A}{VW} \right) \times 100 \]  \hspace{1cm} \text{..........................(3.4)}

Where:
A: oil content (mg) correspondingly to relative absorbency.
VW: volume of water sample, ml
- When oil content is less than 5mg/L, the difference of two results of the sample, which are
tested at parallel, is not more than 20% of the smaller result. When oil content is less than 5-10mg/L, the difference of two results of the sample, which are tested at parallel, is not more than 15% of the smaller result.
- Take the arithmetic mean of the two results from tested samples as the oil content of water sample.
CHAPTER FOUR

Results and Discussions

4.1 Results

The waste treatment unit operates such that the wastewater is firstly neutralized of the alkaline and acidic contaminants then followed by skimming of oil from the water. Secondly the wastewater is sent to a biological treatment unit for further treatment to get rid of other polluting materials.

Ten samples from each of the wastewaters are taken and then analyzed. The results of analysis of wastewater before treatment are shown in Tables 4.1 and results of analysis after treatment are given in Table 4.2.

Poly aluminum chloride (PAC): is used as a coagulant. This coagulant is used to reduce the SS (suspended solid) in final treated water. One of the advantages of PAC that it works in a wide pH range (6-9) COD, thus wide range removal efficiency (40%-71%) has been obtained with different pH and PAC doses. Results of effluent analysis are shown in the following graphs.

Table 4.1: Result of Analysis of Wastewater before treatment

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>7.65</td>
<td>7.98</td>
<td>7.71</td>
<td>7.50</td>
<td>7.65</td>
<td>8.03</td>
<td>8.20</td>
<td>8.54</td>
<td>8.78</td>
<td>8.81</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>2558.0</td>
<td>2776.0</td>
<td>1670.0</td>
<td>1406.0</td>
<td>2076.0</td>
<td>1824.0</td>
<td>1798.0</td>
<td>2392.0</td>
<td>1764.0</td>
<td>2850.0</td>
</tr>
<tr>
<td>Oil content</td>
<td>mg/l</td>
<td>307.25</td>
<td>385.8</td>
<td>219.08</td>
<td>368.75</td>
<td>225.74</td>
<td>731.84</td>
<td>255.38</td>
<td>551.78</td>
<td>329.49</td>
<td>238.54</td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/l</td>
<td>59.01</td>
<td>65.77</td>
<td>40.71</td>
<td>38.85</td>
<td>41.32</td>
<td>65.16</td>
<td>23.42</td>
<td>47.08</td>
<td>57.76</td>
<td>23.85</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>mg/l</td>
<td>22.8</td>
<td>12.5</td>
<td>12.1</td>
<td>24.5</td>
<td>11.0</td>
<td>6.8</td>
<td>4.9</td>
<td>5.8</td>
<td>4.4</td>
<td>7.4</td>
</tr>
<tr>
<td>Sulfide</td>
<td>mg/l</td>
<td>6.24</td>
<td>7.76</td>
<td>2.72</td>
<td>2.64</td>
<td>9.04</td>
<td>8.88</td>
<td>4.56</td>
<td>3.20</td>
<td>3.60</td>
<td>3.76</td>
</tr>
</tbody>
</table>
### Table 4.2: Analysis Results of Treated Wastewater

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>7.88</td>
<td>7.65</td>
<td>7.59</td>
<td>8.39</td>
<td>7.70</td>
<td>*10.78</td>
<td>7.77</td>
<td>7.78</td>
<td>7.56</td>
<td>7.52</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>71.0</td>
<td>109.0</td>
<td>82.0</td>
<td>76.0</td>
<td>164.0</td>
<td>*3132.0</td>
<td>125.0</td>
<td>90.0</td>
<td>95.0</td>
<td>89.0</td>
</tr>
<tr>
<td>Oil</td>
<td>mg/l</td>
<td>10.32</td>
<td>11.23</td>
<td>1.22</td>
<td>7.95</td>
<td>15.37</td>
<td>*690.80</td>
<td>5.51</td>
<td>2.87</td>
<td>3.30</td>
<td>2.41</td>
</tr>
<tr>
<td>content</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>mg/l</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.74</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.69</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>mg/l</td>
<td>0.50</td>
<td>0.80</td>
<td>0.80</td>
<td>1.50</td>
<td>1.80</td>
<td>*8.30</td>
<td>7.20</td>
<td>4.70</td>
<td>5.70</td>
<td>5.80</td>
</tr>
<tr>
<td>Sulfur</td>
<td>mg/l</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>*10.72</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>SS</td>
<td>mg/l</td>
<td></td>
<td></td>
<td></td>
<td>78.00</td>
<td></td>
<td></td>
<td></td>
<td>65.00</td>
<td></td>
<td>81.00</td>
</tr>
</tbody>
</table>

The Average Analysis of Water Samples for the period First of February to Thirteen of March 2016 are compiled and given in Table 4.3

*This is an off point because of a mistake in the analysis equipment discarded from calculations.
Table (4.3): Average Analysis of Water Samples for the period
1st of February to 30 of March 2016

<table>
<thead>
<tr>
<th>Item</th>
<th>Unit</th>
<th>Average IN</th>
<th>Average OUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>7.84</td>
<td>7.75</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>2153.93</td>
<td>150.80</td>
</tr>
<tr>
<td>BOD</td>
<td>mg/l</td>
<td>-</td>
<td>21.92</td>
</tr>
<tr>
<td>Oil content</td>
<td>mg/l</td>
<td>548.50</td>
<td>16.39</td>
</tr>
<tr>
<td>Phenol content</td>
<td>mg/l</td>
<td>70.76</td>
<td>0.19</td>
</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>mg/l</td>
<td>15.41</td>
<td>6.45</td>
</tr>
<tr>
<td>Suspended solid</td>
<td>mg/l</td>
<td></td>
<td>51.00</td>
</tr>
<tr>
<td>Sulfide Content</td>
<td>mg/l</td>
<td>4.53</td>
<td>0</td>
</tr>
</tbody>
</table>

4.2: Environmental Regulations:

Regulations on water pollution, air pollution and noise have been issued by Sudanese Standards and Meteorological Corporation in 2002. Also the World Bank sets limits to water pollution.

a- World Bank Limits

World Bank limits for direct discharges of treated industrial effluents to surface waters are shown in appendix

b- Sudanese Standards and Metrology Organization (SSMO)

Sudanese specifications of the pollutant concentration in the liquid waste generated from oil refineries and petrochemical industries are shown in appendix

The results of the analysis of the samples of wastewaters as well as the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining are plotted in figure 4.1 for pH, Fig.4.2 for COD, Fig 4.3 for Oil content, Fig 4.4 for phenol contents, and Fig 4.5 for sulfide and Fig 4.6 for ammonia.
**Figure 4.1:** pH compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining

![pH Comparison Graph](image1)

**Figure 4.2:** COD (mg/l) compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining

![COD Comparison Graph](image2)
**Figure 4.3:** Oil Content (mg/l) compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining.

**Figure 4.4:** Phenol Content (mg/l) compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining.
Figure 4.5: Sulfide (mg/l) compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining.

Figure 4.6: Ammonia Nitrogen (mg/l) compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining.
4.3 Discussion

The analysis of samples and their comparison with local and international standards were done and it is noticed that:

(i) **pH:** The pH values of wastewater are reduced on the average from 7.84 to 7.75 after treatment. This value satisfies the Sudanese and International Standards.

(ii) **Chemical Oxygen Demand:** The COD values of waste water are reduced on the average from 2153.993 mg/l to 150.80 mg/l after treatment. This value satisfies the Sudanese standers but does not meet International standards.

(iii) **Biochemical Oxygen Demand:** The BOD values of wastewater are reduced to 21.92 mg/l after treatment. This value is satisfying the Sudanese and International standards.

(iv) **Oil Content:** The Oil Content values of waste water are reduced on the average from 548.50 mg/l to 16.39 mg/l after treatment. This value is not satisfying both the Sudanese and International Standards.

(v) **Phenol Content:** The Phenol Content values of wastewater are reduced on the average from 70.76 mg/l to 0.19 mg/l after treatment. This value is satisfying the Sudanese Standards.

(vi) **Sulfide Content:** The sulfide values of wastewater are reduced on the average from 4.53 mg/l to 0 (zero) after treatment, this meets the Sudanese and International standards.

(vii) **Suspended Solids:** The Suspended Solid values of wastewater are reduced on the average 51.00 mg/l after treatment. This value is satisfying the Sudanese and International standards.
Chapter Five
Conclusions and Recommendations

5.1 Conclusions

Petroleum refineries produce large amounts of wastewater that requires treatment. These waters come from many units in the refinery such as distillation columns, heat exchangers and the desalting unit. All the wastewaters from the different sources are collected together and then sent to the physical, chemical and biological treating units. The chemical and/or microbial contamination of wastewater of oil refineries is an environmental hazard.

Effluent wastewaters were tested - standard tests - for the following properties: pH, COD, BOD, Phenol Content, Oil content, NH$_3$-N and Suspended Solid.

This study shows that the majority of the tests that were conducted, whether physical testing, chemical or biological for Khartoum Refinery Company effluents comply with the Sudanese and World Bank standard limits; except that the phenol and oil content values are not conforming to that of the Sudanese Specifications. It also found that the COD and the Oil Contents are off the International Standards.

5.2 Recommendations

- After this study, analysis and reviewal of the current methods of treatment in the refinery, it became obvious that it is necessary to add more processing units such as membrane separation processes.
- It is recommended to search for ways and means of the reduction of process water as well as reuse and recycling of the treated water.
- It is recommended to install clarifiers after DAF and before entering water to biochemical pond to increase the efficiency of the specification of effluent.
References


3- P.N. Gammelgard Water Pollution Control In Petroleum Refineries In The United States Public and Environmental Affairs. 1101 17th Street N.W, Washington, D.C.,20036 1-10.

4- Jin Shangium, “ 1.0 Mt/a Sour water stripping operation procedure”, KRC 2010


6- National Geographic Teachers, “ Geography Reflections on water” November.1992


Appendices
Appendix (A)

Table A: Sudanese Limits for Industrial Effluents Discharge (standard 174/2008-liquid industrial waste)

<table>
<thead>
<tr>
<th>NO</th>
<th>Indicator</th>
<th>Symbol</th>
<th>Unit</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>pH</td>
<td>pH</td>
<td></td>
<td>6-9</td>
</tr>
<tr>
<td>2</td>
<td>Chemical oxygen demand</td>
<td>COD</td>
<td>mg/l</td>
<td>150</td>
</tr>
<tr>
<td>3</td>
<td>Biochemical oxygen demand</td>
<td>BOD</td>
<td>mg/l</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>Oil and grease</td>
<td>O&amp;G</td>
<td>mg/l</td>
<td>5</td>
</tr>
<tr>
<td>5</td>
<td>Total suspended solids</td>
<td>TSS</td>
<td>mg/l</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Phosphorus</td>
<td>P</td>
<td>mg/l</td>
<td>4</td>
</tr>
<tr>
<td>7</td>
<td>Ammonic nitrogen</td>
<td>N_NH₄</td>
<td>mg/l</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>Sulfide</td>
<td>S⁻²</td>
<td>mg/l</td>
<td>0.1</td>
</tr>
<tr>
<td>9</td>
<td>Sulfate</td>
<td>SO₄</td>
<td>mg/l</td>
<td>350</td>
</tr>
<tr>
<td>10</td>
<td>Aluminum</td>
<td>Al</td>
<td>mg/l</td>
<td>5</td>
</tr>
<tr>
<td>11</td>
<td>Arsenic</td>
<td>As</td>
<td>mg/l</td>
<td>0.3</td>
</tr>
<tr>
<td>12</td>
<td>Barium</td>
<td>Ba</td>
<td>mg/l</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>Phenol</td>
<td>C₆H₅OH</td>
<td>mg/l</td>
<td>0.002</td>
</tr>
<tr>
<td>14</td>
<td>Copper</td>
<td>Cu</td>
<td>mg/l</td>
<td>0.5</td>
</tr>
<tr>
<td>15</td>
<td>Iron</td>
<td>Fe</td>
<td>mg/l</td>
<td>5</td>
</tr>
<tr>
<td>16</td>
<td>Lead</td>
<td>Pb</td>
<td>mg/l</td>
<td>0.2</td>
</tr>
<tr>
<td>17</td>
<td>Magnesium</td>
<td>Mg</td>
<td>mg/l</td>
<td>100</td>
</tr>
<tr>
<td>18</td>
<td>Organic Nitrogen</td>
<td>N(organic)</td>
<td>mg/l</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Pollutants</td>
<td>Unit</td>
<td>Guideline Value</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---------------------</td>
<td>---------</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Mercury</td>
<td>Hg</td>
<td>mg/l</td>
<td>0.2</td>
</tr>
<tr>
<td>20</td>
<td>Zinc</td>
<td>Zn</td>
<td>mg/l</td>
<td>5</td>
</tr>
<tr>
<td>21</td>
<td>Selenium</td>
<td>Se</td>
<td>mg/l</td>
<td>20</td>
</tr>
<tr>
<td>22</td>
<td>Boron</td>
<td>Bo</td>
<td>mg/l</td>
<td>1.0</td>
</tr>
<tr>
<td>23</td>
<td>Silver</td>
<td>Ag</td>
<td>mg/l</td>
<td>0.05</td>
</tr>
<tr>
<td>24</td>
<td>Sodium</td>
<td>Na</td>
<td>mg/l</td>
<td>300</td>
</tr>
<tr>
<td>25</td>
<td>Total count of bacteria</td>
<td>Aerobic plate count</td>
<td>Counts/100 ml</td>
<td>1000</td>
</tr>
</tbody>
</table>

Appendix (B)

Table B: World Bank Limits for Direct Discharges of Treated Industrial Effluents to Surface Water

<table>
<thead>
<tr>
<th>Pollutants</th>
<th>Unit</th>
<th>Guideline Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>pH</td>
<td>6-9</td>
</tr>
<tr>
<td>BOD</td>
<td>mg/l</td>
<td>30</td>
</tr>
<tr>
<td>COD</td>
<td>mg/l</td>
<td>125</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>mg/l</td>
<td>10</td>
</tr>
<tr>
<td>Total Phosphorus</td>
<td>mg/l</td>
<td>2</td>
</tr>
<tr>
<td>Oil and Grease</td>
<td>mg/l</td>
<td>10</td>
</tr>
<tr>
<td>Total Suspended Solid</td>
<td>mg/l</td>
<td>50</td>
</tr>
<tr>
<td>Total Count of Bacteria</td>
<td>Count 100 ml</td>
<td>1000</td>
</tr>
</tbody>
</table>
Appendix (C)

**Table C₁:** pH values compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Treated Water</th>
<th>Sudanese Standard</th>
<th>Work Bank Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.65</td>
<td>7.88</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>7.98</td>
<td>7.65</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>7.71</td>
<td>7.59</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>7.50</td>
<td>8.39</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>7.65</td>
<td>7.70</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>8.03</td>
<td>10.78</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>8.20</td>
<td>7.77</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>8.54</td>
<td>7.78</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>8.78</td>
<td>7.56</td>
<td>6-9</td>
<td>6-9</td>
</tr>
<tr>
<td>8.81</td>
<td>7.52</td>
<td>6-9</td>
<td>6-9</td>
</tr>
</tbody>
</table>

**Table C₂:** COD mg/l compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Treated Water</th>
<th>Sudanese Standard</th>
<th>Work Bank Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>2558.0</td>
<td>71.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>2776.0</td>
<td>109.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>1670.0</td>
<td>82.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>1406.0</td>
<td>76.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>2076.0</td>
<td>164.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>1824.0</td>
<td>3132.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>1798.0</td>
<td>125.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>2392.0</td>
<td>90.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>1764.0</td>
<td>95.0</td>
<td>150</td>
<td>125</td>
</tr>
<tr>
<td>2850.0</td>
<td>89.0</td>
<td>150</td>
<td>125</td>
</tr>
</tbody>
</table>
Table C3: Oil Content mg/l compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Treated Water</th>
<th>Sudanese Standard</th>
<th>Work Bank Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>307.25</td>
<td>10.32</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>385.80</td>
<td>11.23</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>219.08</td>
<td>10.22</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>368.75</td>
<td>7.95</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>225.74</td>
<td>15.37</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>731.84</td>
<td>690.80</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>255.38</td>
<td>5.51</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>551.78</td>
<td>2.87</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>329.49</td>
<td>3.30</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>238.54</td>
<td>2.41</td>
<td>5</td>
<td>10</td>
</tr>
</tbody>
</table>

Table C4: Phenol Content mg/l compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Treated Water</th>
<th>Sudanese Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>59.01</td>
<td>0.00</td>
<td>0.002</td>
</tr>
<tr>
<td>65.77</td>
<td>0.00</td>
<td>0.002</td>
</tr>
<tr>
<td>40.71</td>
<td>0.00</td>
<td>0.002</td>
</tr>
<tr>
<td>38.85</td>
<td>0.74</td>
<td>0.002</td>
</tr>
<tr>
<td>41.32</td>
<td>0.00</td>
<td>0.002</td>
</tr>
<tr>
<td>65.16</td>
<td>0.00</td>
<td>0.002</td>
</tr>
<tr>
<td>23.42</td>
<td>0.00</td>
<td>0.002</td>
</tr>
<tr>
<td>47.08</td>
<td>0.69</td>
<td>0.002</td>
</tr>
<tr>
<td>57.76</td>
<td>0.00</td>
<td>0.002</td>
</tr>
<tr>
<td>23.85</td>
<td>0.75</td>
<td>0.002</td>
</tr>
</tbody>
</table>
**Table C₅**: Sulfide Content mg/l compared with the permissible limits of World Bank and Sudanese specifications for liquid waste effluent from petroleum refining

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Treated Water</th>
<th>Sudanese Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.24</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>7.76</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>2.72</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>2.64</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>9.04</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>8.88</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>4.56</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>3.20</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>3.60</td>
<td>0.00</td>
<td>0.1</td>
</tr>
<tr>
<td>3.76</td>
<td>0.00</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Table C₆**: Ammonia Nitrogen mg/l analysis results

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Treated Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.8</td>
<td>0.5</td>
</tr>
<tr>
<td>12.5</td>
<td>0.8</td>
</tr>
<tr>
<td>12.1</td>
<td>0.8</td>
</tr>
<tr>
<td>24.5</td>
<td>1.5</td>
</tr>
<tr>
<td>11.0</td>
<td>1.8</td>
</tr>
<tr>
<td>6.8</td>
<td>8.3</td>
</tr>
<tr>
<td>4.9</td>
<td>7.2</td>
</tr>
<tr>
<td>5.8</td>
<td>4.7</td>
</tr>
<tr>
<td>4.4</td>
<td>5.7</td>
</tr>
<tr>
<td>7.4</td>
<td>5.8</td>
</tr>
</tbody>
</table>