# Chapter One
## Introduction

### 1.1 General

The word environment comes from the French verb environner (to surround) and means surroundings or something that surrounds **(Azad, 2015)**. The term environment, according to **(Gilpin, 1976)**, is the region, surroundings, or circumstances in which anything exists; everything external to the organisms . Environment embraces all those disciplines which are concerned with the physical, chemical, political, social, cultural, biological and even technological surroundings in which all kinds of organisms live **(allaby, 2002)**. The environment consists of air, water, earth, and life which are briefly described below **(Manahan, 2000)**. Atmosphere, hydrosphere, geosphere, biosphere, and anthrosphere (technology) are strongly interconnected as shown in (Figure 1.1).

(a) **The atmosphere,** is the thin layer of gases that cover Earth's surface. In addition to its role as a reservoir of gases, the atmosphere moderates Earth's temperature, absorbs energy and damaging ultraviolet radiation from the sun, transport energy away from equatorial regions, and serves as a pathway for vapor-phase movement of water in the hydrologic cycle.

(b) **The hydrosphere,** contains Earths water. Over 97% of Earths water is in oceans, and most of the remaining fresh water is in the form of ice. Therefore, only a relatively small percentage of the total water on Earth is actually involved with terrestrial, atmospheric, and biological processes. Exclusive of seawater, the water that circulates through environmental processes and cycles occurs in the atmosphere, underground as groundwater, and as surface water in streams, rivers, lakes, ponds, and reservoirs.

(c)**The geosphere**, or solid Earth, is that part of the Earth upon which humans live and from which they extract most of their food, minerals, and fuels. The geosphere consist of the solid earth, including soil, which supports most plant life. The part of
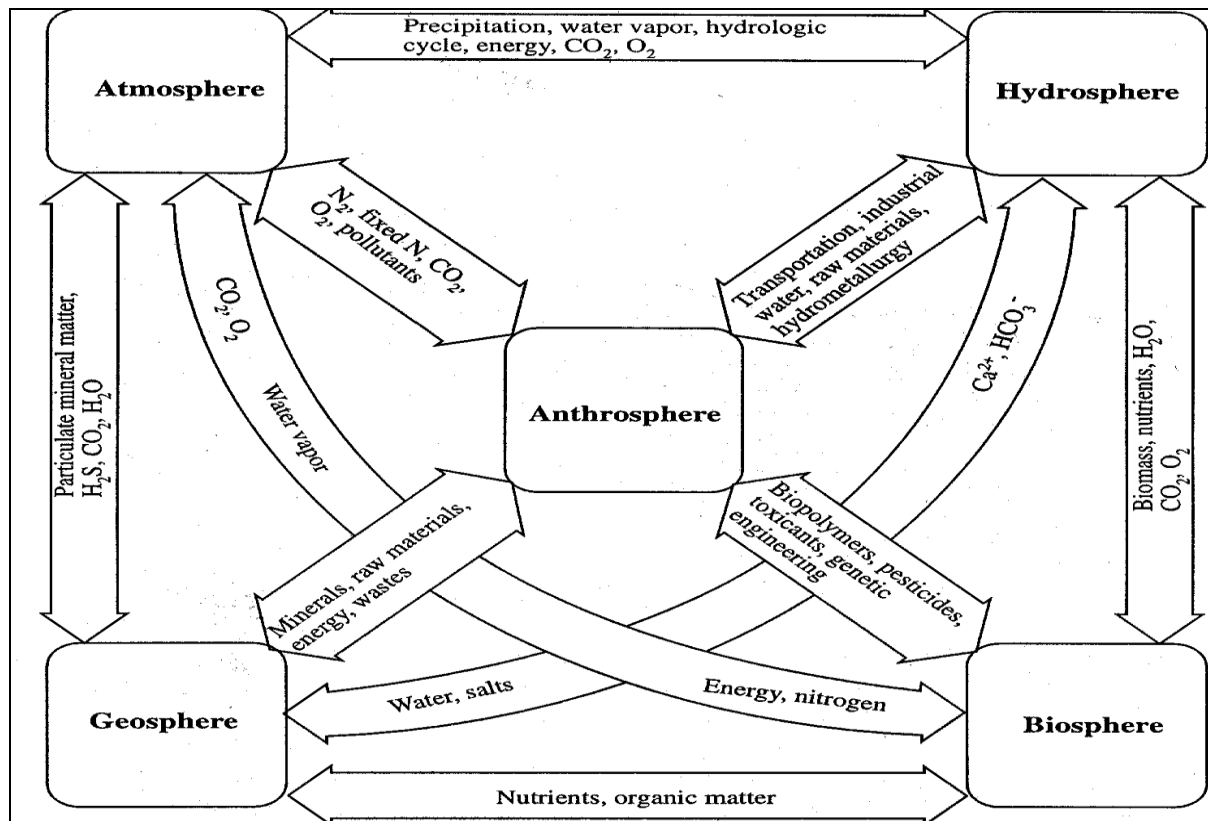
**Figure 1.1 :** Illustration of the close relationships among the air, water, and earth environments with each other and with living systems, as well as the tie-in with technology (the anthrosphere). Source: Manahan, (2000).

the geosphere that is directly involved with environmental processes through contact with the atmosphere, the hydrosphere, and living things is the solid lithosphere which varies from 50 to 100 km in thickness. The most important of it insofar as interactions with the other spheres of the environment are concerned is its thin outer skin composed largely of lighter silicate-based minerals and called the crust.

**(d) The biosphere,** is that part of the environment consisting of all living entities including plants, animals, organisms, and living biological material. Virtually all of the biosphere is contained by the geosphere and hydrosphere in the very thin layer where these environmental spheres interface with the atmosphere. The biosphere strongly influences, and in turn strongly influenced by, the other parts of the

environment. It is believed that organisms were responsible for converting Earth's original reducing atmosphere to an oxygen-rich one a process that also resulted in the formation of massive deposits of oxidized minerals, such as iron in deposits of $Fe_2O_3$.

## 1.2 Environmental Pollution

As environmental awareness increases, industries and businesses become obsessed in assessing how their activities affect the environment. The society has become concerned about natural resource depletion and environmental degradation issues **(Curran, 2006; Chen *et al.*, 2010; Tehrani *et al.*, 2010)**. Pollution sources are created by man, thus pollution is an increment added by man to bio-geo-chemical cycles as an inevitable consequence of human activities such as industry, agriculture, transport, military activities, domestic effluents, introducing various types of wastes to the environment. Any substance in water, soil, or air that degrades the natural quality of the environment, offend the senses of sight, taste, or smell, or cause a health hazard is considered as pollutant. The usefulness of the natural resource is usually impaired by the presence of pollutants and contaminants. **Hutton *et al.* (1986)** estimated the quantities of heavy trace elements inputs to the land in the UK as a result of human activities that include use of articles containing the elements ions and steel production, fuel consumption, cement industry, phosphate, municipal waste disposal, sewage and sewage sludge disposal in tons per year, Cd (8990) Pb (48316), Hg (113) and As (1530). **Henning and Mangun (1989)**, defined pollution as "the presence in the environment of matter or energy whose nature, location or quantity produces environmental effects undesirable for humans".

A waste is a movable object which has no direct use and is discharged permanently **(Bastone, 1989)**. Waste materials could be in the solid, liquid or gaseous form, and according to their nature and characteristics and the effects produced can be described for example; as toxic and/or hazardous. Hazardous wastes are any wastes

or combination of wastes which pose a substantial present or potential hazard to human or living organisms, because they are lethal, non- degradable, persistent in nature, can be biologically magnified, or otherwise cause or tend to cause detrimental cumulative effects **(powers, 1976)**. Substances are considered hazardous waste if they exhibit one or more of the following characteristics, **(Vesilind and Pereira, 1980)**.

•Ignitable: Ignitable wastes generally are liquids with a flash point below 60ºC

•Corrosive: Corrosive wastes are generally aqueous wastes with a pH less than or equal 2 or greater than or equal to 12.5.

•Reactive: Reactive wastes are those wastes that are unstable, explosive, capable of detonation, or react violently with water.

•Toxic: Containing substances that are poisonous.

The most common sources of hazardous wastes are industrial, agricultural, household and medical wastes. Hazardous wastes can be controlled by source reduction, recycling, treatment and proper disposal.


Environmental pollution is a matter of great concern and has been accepted as a global problem because of its adverse effects on human health, plants, animals and exposed materials. Because humans are at the top of the food chain, they are particularly vulnerable to the effects of non-degradable pollutants. This was clearly illustrated in the 1950s and 1960s when 400 people of the residents living near Minamata bay, Japan, died before authorities discovered that a local industry had released mercury into the bay. This highly toxic element accumulated in the bodies of local fish and eventually in the bodies of people who consumed the fish. More recently research has revealed that many chemical pollutants, such as DDT and PCBs, mimic sex hormones and interfere its human body's reproductive and developmental functions. These substances are known as endocrine disrupters. Pollution also has a dramatic effect on natural resources. Ecosystems such as forests, wetlands, coaral reefs, and rivers performed many important services for

earth's environment. They enhance water and air quality, provide habitat for plants and animals and provide food and medicines. Any or all of these ecosystem functions may be impaired or destroyed by pollution. Moreover because of the complex relationships among the many types of organisms and ecosystems, environmental contamination may have far–reaching consequences that are not immediately obvious or that are difficult to predict. Another major effect of pollution is the tremendous cost of pollution cleanup and prevention.

In addition to its effects on economy, health, and natural resources, pollution has social implications. Research has shown that low–income populations and minorities do not receive the same protection from environmental contamination as do higher- income communities. Toxic waste incinerators, chemical plants, and solid waste dumps are after located in low–income communities because of a lack of organized, informed community involvement in municipal decision–making processes. The effect of pollution do not confine  to the global level only, but can create regional and/or global problems such as climatic changes resulting from global warming due to the greenhouse effect. Pollution exists in many forms and affects many different aspects of Earth's environment. Point– source pollution comes from specific, localized, and identifiable sources, such as sewage pipelines or industrial smokestacks. Nonpoint –source pollution comes from uncontained sources, such as contaminated water runaff from urban areas or automobile emissions.  Primary effects of pollution occur immediately after contamination occurs, such as the death of marine plants and uildilfe after an oil spill at sea. Secondary effects may be delayed or may perrist in the environment into the future, perhaps going unnoticed for many years. Pollution falls into six main types :

**1.2.1 Air pollution**

Air pollution refers to the introduction of physico-chemical or biological materials into the atmosphere that may cause harm or discomfort to humans or other living organisms, or deterioration of the natural environment **( Gurjar *et al.*, 2010).** US

EPA define air pollution as the presence of contaminants or pollutant substances in the air that interfere with human health or welfare, or produce other harmful environmental effects **(US EPA, 2007)**. Globaal warming is the most urgent environmental challenge of the 21st century. Because of the world's continued dependence on fossil fuels as an energy source, greenhouse gas levels are steadily increasing in the atmosphere and warming the earth and consequentely causing the worldwide destruction of ecosystems and extinction of species **(Casper, 2010)**. Air pollution takes many forms and effects numerous natural processes and human health. It can be physical such as the energy from the ultraviolet (UV) light. Our exposure to this physical contamination was brought about by chemical contamination. The release of chemicals, such as FCCs into the atmosphere decrease the ozone concentrationand increase the amount of UV radiation at the earth's surface which is associated with an increase in the incidence of skin cancer **(Vallero, 2008)**.

## 1.2.2 Water pollution

Parker **(1981)** defined water pollution as (any change in natural waters which may impair their further use, caued by the introduction of organic or inorganic substances, or a change in temperature of the water).The major sources of water pollution may be classified as domestic, industrial, agricultural and shipping wastewaters. Agricultural wastes pollute waters through eutrophication which can cause the death of fish and other a quatic life. Many rivers and fresh- water streams are seriousl polluted by industrial wastes which are highly toxic to animals. A steep rise in fish mortality was reported in the river Sone (India) owing to the chlorine content chemical wastes discharged by factories near the site. Oil pollution from accidents involving large tankers and affshore drilling rigs has attracted international attention. Erosion, the wearing away of topsoil by wind and rain, and air pollution also contribute to water pollution.

The report on Europe,s Environment summarized by Burke **(1996)**, reveals that about 65% of Europe,s population depends on groundwater, a resource described as overexploited in almost 60% of Europian industrial and urban centres and threatened by pollutants. The European Union standard for total pesticides is exceeded in soil water in 60-75% of agricultural land, while river and lake eutrophication caused by excessive phosphorus and nitrogen from agricultural, domestic, and industrial effluents is a problem across most of Europe. However, the effects of contaminants or pollutants on freshwater depend upon their chemical, physical, and biological properties, their concentrations and duration of exposure **(Harison, 1999)**.

### 1.2.3 Land pollution

Land (soil) pollution is defined as the build-up in soils of persistent toxic compounds, chemicals, salts, radioactive materials, or disease-causing agents which have adverse effects on plant growth and animal health and turn the soil unfit for man's needs **(Chirila and Draghici, 2008)**. Soil could be polluted by introduction of substances, biological organisms, or energy into the soil, resulting in a change of the soil quality, which is likely to affect the normal use of the soil or endangering public health and the living environment. Soil pollution is caused by the introduction of pollutants either directly as ; for example pesticides, excess and synthetic fertilizers which are non biodegradable and accumulate in the soil system and hence destroy useful organisms such as bacteria, accidental spillage of chemicals, and disposal of solid and liquid wastes, and indirectly such as the contribution from air pollution and polluted drainage waters.

### 1.2.4 Noise pollution

Is the condition where noise has characteristics and duration injurious to public health and welfare, or which unreasonably interfere with the comfortable enjoyment of life and property in such areas as are affected by the noise **(Salvato, 1982)**. Transportation vehicles, aircrafts, trucks and industries all producing excessive noise. Noise pollution is environmental and work place problem.

Excessive noise can cause permanent or temporary loss of hearing, affects the circulatory and nervous system. While noise was considered just another annoyance in a polluted world, not much attention was given to it. We now have enough data to show that it is a definite health hazard and should be numbered among our more serious pollutants **(Peirce _et al.,_ 1997)**.

## 1.2.5 Radioactive pollution

It is the introduction of radioactive substances to the waters, soil, and air, resulting in environmental damage and threatening human health. The major sources of radioactive pollution are nuclear power plants, nuclear weapons, transportation, disposal of nuclear wastes, and uranium mining.

## 1.2.6 Thermal pollution

Thermal pollution is waste heat released to the environment as the unavoidable by product from various facilities such as nuclear power plants, industrial effluents, domestic sewage and electric power plants. This waste heat when released to a water body, harms man, animal, and aquatic life **(Hill, 1972)**. Increased temperature in water has a significant impact on the growth and activity of ecologicals life. Also it greatly affects the solubility of essential gases such as oxygen in water and subsequently influences the oxidation of organic matter present in water streams **(Tomar, 1999)**.

## 1.3 Industrial Pollution

The first stage of economic developement typically witness the rapid growth of industrial activity which provided a source of rapidly expanding income, but declining environmental quality in densely populated areas. Energy consumption has a significant impact on our natural environment. Recently, a consensus has arisen that there is clear evidence that climate change is caused by human activity, mostly related to the use of energy **(Morvay and Gvosdenac, 2008)**. The biggest environmental impacts in industry come from the use of fossil fuels(oil and coal) which are converted into useful energy through a combustion process resultingin significant impact on the natural environment and generate emissions into the air,

water, and soil. Industries produce large volumes of wastes that may include a wide variety of chemicals containing most toxic pollutants. It has been estimated that there are over 300,000 water-using factories in the United States **(Parker and Qasim, 2006)**.

When new industries are pollution –intensive, their emission can increase local ambient pollution concentrations to harmfull levels. The cost of industrial pollution ,which became a serious problem in many developing countries, include serious damage to human health and ecosystems. Industrial waste products have contaminated drinking water and, in more severe cases caused evacuation of homes. A large number of waterways are near biological death from excessive discharge of organic pollutants. In many urban areas, atmospheric concentrations of pollutants such as suspended particulates and sulphur dioxide routinely exceed who safety standards by very large margins. The sectoral composition of industrial activity has an important effect on its average pollution intensity. Industrial processes differ greately in their production of waste residuals which, inturn have varying potential for creating environmental damage. Even in well-regulated economies, these factors cause significant intersectoral differences in pollution intensity.

## 1.4 Petroleum Refining Industry

Despite the development of new technologies and products such as biofuels, oil still has great commercial importance and will continue to play a critical role in the global energy industry for many decades, especially with the discovery of the pre-salt layer **(Alexandre *et al.,* 2015)**. The petroleum industry is organized into four broad sectors: exploration and production of crude oil and natural gas; transport; refining; and marketing and distribution. Petroleum refineries and petrochemical plants are the kingpins of the petroleum industry. They are one of the barons of the industrial sector globally and became the kingpin in the sudanese industrial sector.

Petroleum refining can be defined as the physical, thermal, and chemical separation of crude oil into its major distillation fractions which are then further processessed through a series of separation and conversion step into finished petroleum products **(US EPA, 1995)**. A petroleum refinery is the facility where this process takes place through an organized and coordinated arrangement of manufacturing process that constitute the refinery. Although the processing systems of oil refineries have various degrees of sophistication, they all have the common task of splitting up crude oil into the range of petroleum products required by a modern industrialized society. The primary products of the industry are fuels: motor gasoline, diesel and distillate fuel oil, kerosene, liquefied petroleum gas, jet fuel, residual fuel oil and coke; finished non-fuel products: solvents lubricating oils, grease, petroleum wax, petroleum jelly and asphalt; chemical industry feed stocks: naphtha, ethylene, propylene, butylenes, benzene, toluene and xylene. About 90% of the petroleum product used, for example, in the united states are fuels with motor gasoline accounting for about 43% of the total **(Cheremisinoff, 2002)**. The petrochemical industries derive its feedstock from refinery processes which are then converted into valuable products such as plastics and resins, synthetic rubber, materials for agriculture including agrochemicals and cleaning agens, which further surve as materials for downstream industries.

While petroleum and refining and petrochemical industries are most desirable for national development and improved quality of life, the unwholesome and environmentally unacceptable pollution effects of the wastes from these industries have been reported worldwide **(Ruiz-Ordaz *et al.*, 2001; Chang *et al.*, 1998)**. The refining industry has been recognized as one of the most polluting industries, which has a significant to the degradation of the environment, because there is a great potential for generation of wastes that comprising gaseous, liquid, and solid materials, most of which are toxic and hazardous. They process extremely high volumes (in 2012 the refining capacity in operation worldwide was 89 million

barrels/day) and are major contributors to pollution, both in volume and in the concentration and toxicity of contaminants **(OPEC, 2013; Diya'Udeen *et al*., 2011)**.

## 1.5 Khartoum Petroleum Refinery

Khartoum Refinery Company (KRC) Limited (Figure 1.2) is a joint venture between China National petroleum Corporation (CNPC) and the Ministry of Energy & Mining (MEM) of Sudan. The refinery srarted operating on May 2000. The main process units are Crude Distillation Unit (CDU ) with maximum design capacity of 2.5 million tons of crude oil per year , Residue Fluidize Catalytic Cracking Unit (RFCC) with a design capacity of 1.800.000 tons a year , Catalytic Reforming Unit (REF) with design capacity of 15 thousand tons per year , and Diesel Hydrotreating Unit (HDT) with 400 thousand tons per year designing capacity, Sour Water stripper with a design capacity of 400 thousand tons per year. The auxiliary utilities at the refinery constitute power generation station 36 megawatt, water purification and pumping, 1500m3/h, and wastewater treatment plant . The crude oil processing capacity is 2.5 million tons per year i.e 50,000 bbl/d, expanded later when CNPC announced in July 2006, the completion of the Khartoum refinery expansion project, which doubled the refinery's capacity from 50,000 bbl/d to 100,000 bbl/d. The refinery processes Nile blend crude, which has a low sulphur content and high fuel-yield. The annual output is 2.2587 million tons of oil products such as unleaded gasoline, kerosene, jet fuel, diesel, fuel oil and liquefied gas.

Sources of wastewater associated with various units are **(Faris and Abdel-Magid, 2003)** :

Crude Tank: Crude oil normally contains traces of water, an average of 0.05% per weight. Therefore, water generated is about 3.75 tons/day; desalting, crude distillation unit (CDU), diesel hydro treating unit (DHT), residue fluid catalytic

cracking, utilities : cooling water system , power station , and boilers; other sources: rain water and cleaning "washing" water.

Caustic wastewater is acid neutralized and discharged into oily wastewater system. Sour water from all processing units is treated in sour water stripping unit with a capacity of 400,000 tone/year then sent into wastewater treatment plant. Oily water and alkaline water are sent to wastewater treatment plant. Sanitary wastewater from living area and offices is treated in cesspool then sent into wastewater treatment plant. Cooling towers water is also discharged into wastewater treatment plant. In the wastewater treatment plant (WWTP) of 300t/h capacity, wastewater received a primary treatment for gravity removal of floatable oil and settling of sludge, and secondary treatment to remove biodegradable pollutants . It is now allowed to enter into monitoring pond and then into oxidation ponds outside the refinery **(Khogali, 2005)**.



**Figure 1.2 :** Aerial view of Khartoum Petroleum Refinery.

## 1.6 Statement of the Problem

Petroleum refineries consume large amounts of water, up to $3m^3$ of water per ton of oil processed **(US EPA, 1980),** in the process of crude oil convertion into useable products such as gasoline and generate by- products, which are harmful to the environment. These by–products or wastes are produced in all forms (i.e., gases, liquids, and solids) and released into the suronding environment. Most of the water utilized in the refinery is discharged as wastewater including process water,cooling water, surface water runoff, and sanitary wastewater .The volume of the wastewater generated is 0.4–1.6 times the volume of processed oil **(Parilti, 2010)**.

Before starting an industrial activity, such as Khartoum refinery, an environmental impact assessment (EIA) should have been carried out to assess the environment in the surrounding area and within the proximity of the refinery. This type of studies that is termed base line study (BLS) serves as a base for comparison and how this industry affects the environment and consequently lead to polices for appropriate waste management and healthy environment. To our knowledge, this study is not performed. On the other hand new globalization polices require industries to comply with international standard organization (ISO) laws before qualifying for international trading. A prerequisite for any big plant such as Khartoum refinery ( and its petrochemical expansion), to succeed with its products in world market is to have a proven and internationally acceptable record with respect to environmental management. Thus, it is important to raise awareness, and have concern about the pollution problems created as a result of generation of effluents from the refinery. It is also of prime importance to emphasise the need for the protection of the environment of the area.Therefore, it is very important to fill the gap at least in effluent assessment by collecting quantitative and qualitative data for monitoring and future studies since, there is a lack in data and no comprehensive study has ever been conducted for the environmental consequences of Khartoum refinery operation.

Algaili and its neighboring villages (rural region), located along the River Nile shore at a distance of about 12 km to the west of Khartoum refinery have a total population of about 25,000 working mostly in wheats, vegetables, fruits, and poultry farms besides grazing. This area supplies the capital, Khartoum, with crops, vegetables, fruits, dairy products, and poultry eggs and meats as well as plants used for feeding animals like cows. The topography of the area shows generally flat land containing a number of isolated hills and soil cover. The whole area is gently dipping westward with a number of shallow, dry wadis draining through the area from high ridges in the East of the refinery towards the River Nile in the western part where the villages and the farms are located. The area is famous of its seasonal streams and frequently is affected by floods. Therefore, the liquid effluents generated from Khartoum refinery, if not treated properly and disposed off in an environmentally acceptable manner, it can cause adverse environmental impacts on the surrounding environment.The underground waters can be contaminated with pollutants carried by the effluents. Also the effluents can be washed with rain runoff, carrying with it, toxic and hazardous substances and other pollutants. The combined waters can find its way to the River Nile and farms located there, through many seasonal streams along short distance (12 km) and hence, there is a great potential for polluting the water, land and farms, and consequently affecting human health in and outside the area through food chain, degrade soil quality, and cause economic loss.

### 1.7 Research Aims and Objectives

The aims of the present work are to:

(1) Assess the quality of the final effluent disposed into the environment and establishment of background base line data for pollution levels.

(2) Assess the potential environmental impacts of the refinery effluents on the area.

To satisfy the above aims, the following Specific objectives are undertaken:

(1) Identification of the wastewater sources and streams.

(2) Analysis of the final discharged effluent, and measure physicochemical pollution parameters and heavy metals Fe, Ni, Cu, Cr, Cd, Ba, Pb, Zn, Ag, and Se to determine their concentration levels.

(3) Investigation of the heavy metals Fe, Ni, Cu, Cr, Cd, Ba, Pb, Zn, Ag, and Se concentrations in the oxidation ponds sediments.

(4) Assessment of the treatment and disposal methods applied.

**1.8 Research Questions**

(1) Is the effluent quality comply with the Sudanese and international standards ?

(2) What is the extent of heavy metals contamination in the oxidation ponds sediments ?

(3) Are the applied treatment and disposal methods efficient enough ?

(4) Are the valuable environmental resources in the study area threatened by the refinery effluents?

(5) What are the ways of solving the problems of effluent quality and disposal method ?

**1.9 Scope of the Study**

This study covers the Northern rural area of Khartoum North Locality in Khartoum State where Khartoum petroleum refinery, a joint venture between China National petroleum Corporation (CNPC) and the Ministry of Energy & Mining (MEM) of Sudan, is located. It includes a study of the refinery's liquid effluent in an attempt to determine its quality as well as a study of heavy metals content of oxidation ponds sediments to determine their concentration levels. The research covered the assessment of the petroleum refining activities especially liquid effluents pathway from generation, inside the refinery, to discharge into the surrounding environment. The biological, physical, and geochemical features data of the area were collected besides experimental data to help in assessment of potential negative impacts with emphasis on environmentally sensitive sites. The research was executed through survey and laboratory designs.

## 1.10 Limitations of the Study

The study has several limitations; amongst which is insufficient accessibility of the crude processing units sites in the refinery due to strict security measures as to who should be allowed into the units area for the purpose of collecting information. Also, some of the research questions were beyond the scope and capability of the employees, such questions concerning wastewater origins, streams, and characteristics. Every attempt to get the administrative staff of KRC to answer these questions met with resistance and lack of cooperation from them. Also sampling activities at the oxidation ponds site met with restrictions , doubts, and hesitations so that samples were sometimes taken in uncomfortable conditions.

Lastly, quantitative literature on oil spill and leak incidents and effluent characteristics , was not sufficiently accessible, and above all, finances are some of the limitations of the study.

## 1.11 Significance of the Study

Petroleum refinery liquid effluents has direct and indirect deleterious effects on the environment of petroleum refining communities and distant  communities respectively. It is a major threat to the survival of the ecological system and human health. A research into quality assessment and management of petroleum refinery liquid effluents will provide information and data base which will help in the elimination and amelioration of the problem of effluent negative impacts, thereby protecting the environment and human health and save the financial loss that these impacts cause and thereby improving the Nations Economy, because the economy of Sudan is dependant on the oil sector since 2000. Also, when it is discovered from the study that liquid effluents from Khartoum Refinery pose a threat to the environment , the results of the finding will be beneficial to the community as it will act as a guide in water resources development, academic growth, and policy formulation.

There was little background data available to help design a study looking at the performance of oxidation ponds and their sediment quality . However, because large and deep oxidation ponds receiving very complicated mixture of various hazardous and toxic chemicals besides bacterial populations, are included in the study area, many complications were expected in terms of  sediment samples collection .The study therefore provided an opportunity to evaluate monitoring methodologies in such ponds environments.

The study will help the researcher uncover critical areas in environmental management of industrial wastes, and in particular, petroleum refining wastewater quality and management, that was not explored in the area. Above all, the great significance and high value of the present study is attributed to that it is the first and only comprehensive study assessing environmental aspects of a petroleum refinery liquid effluents in Sudan.

## 1.12 Description of the Study Area

The study area, the Northern rural area, is located around Khartoum petroleum refinery in Khartoum North locality area of Khartoum State. Khartoum State (Figure 1.3 ) is bounded on the North by River Nile State, North-West by Northern State , West by North Kordofan State , South by the  States of White Nile and Gezira, South- East by Gedaref State, and East by Kassala State. It lies between longitudes 31.5 to 34 °E and latitudes 15 to 16 °N. Although it is the smallest state by area (22,142 km$^2$), it is the most populous (5,274,321 in 2008 census), **(CBS, 2009)**. The city of Khartoum, which is the capital of the state as well as the national capital of Sudan , is located in the heart of Sudan at the confluence of the White Nile and the Blue Nile, where the two rivers unite to form the River Nile which continues to flow North passing through the study area and the States of  River Nile and Northern  before entering the Mediterranean Sea at  Egypt.
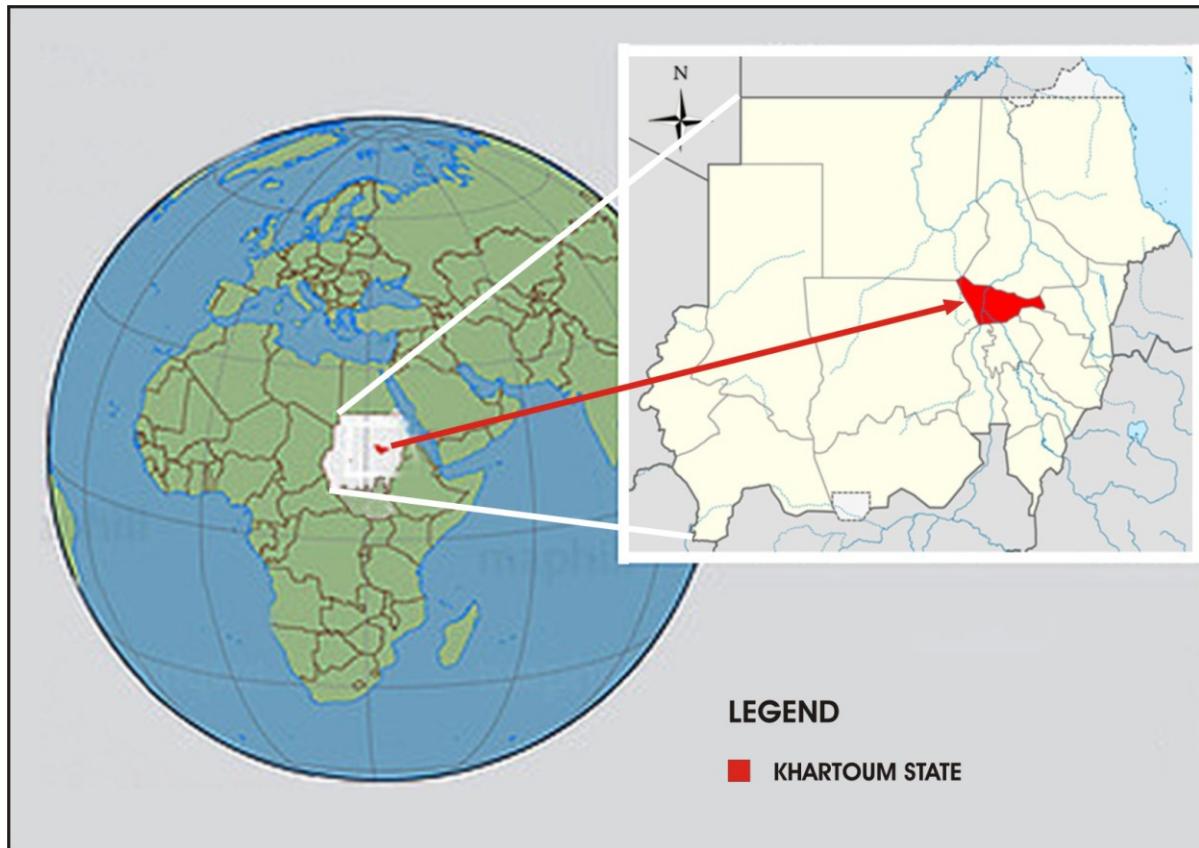
**Figure 1.3 :** The map of Sudan showing the location of Khartoum State.

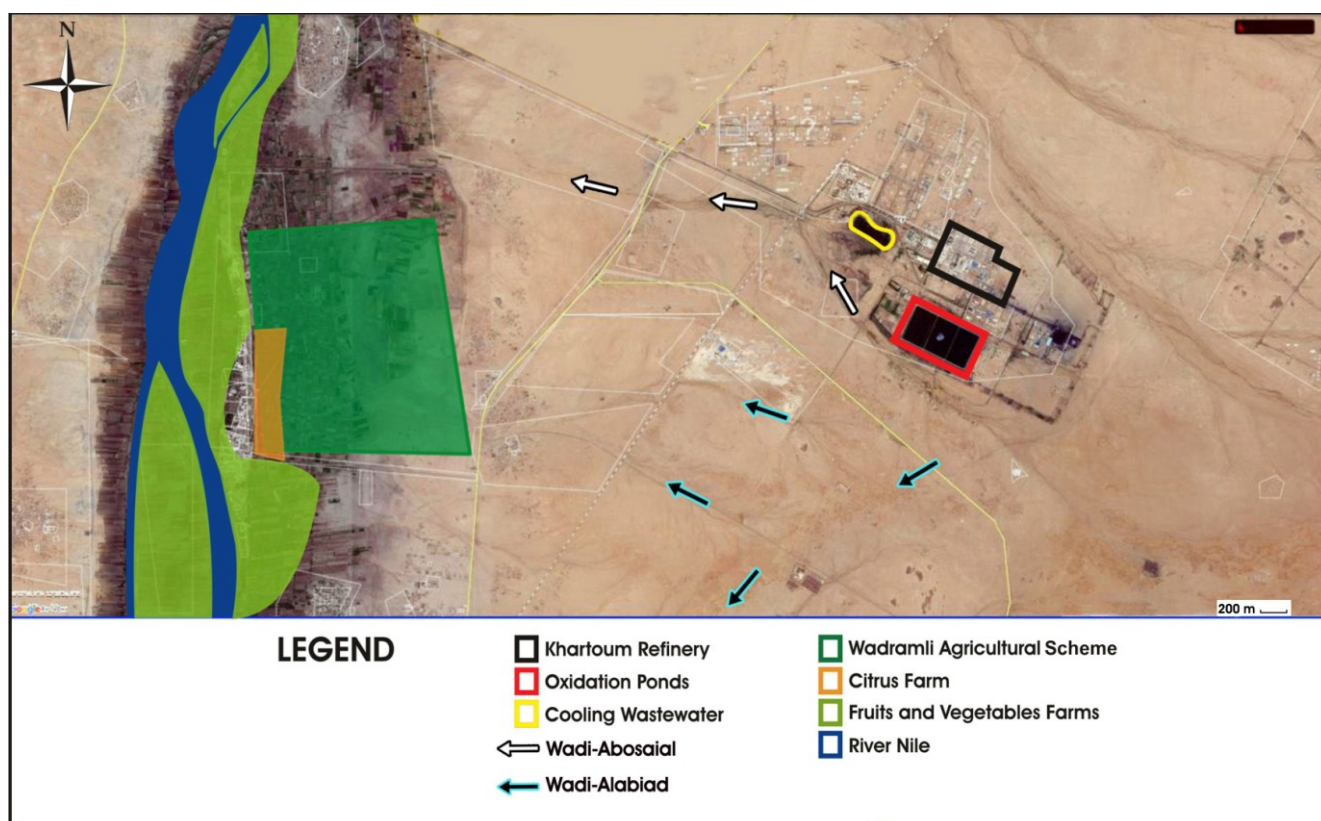Source: Google Maps Website- Modified.

The study area (Figure1.4), which is a typical rural region lies between longitudes 32.550173°-32.698488° E and latitudes 15.779038°-16.179397° N, comprises Khartoum Refinery , Algaili town, and its neighboring villages along and near the River Nile banks icluding farms sites. The villages that makes up of the study area are Abohalima, Faki-Hashim, Alzakiab, Alhassania,  Alkhoglab, Alkabashi, Alsagai, Altomaniat, Elnaia, Aldawm, Wawissi, Wadramli, Almanofalab, Alnikheila, Altikaina, Dabak, and Garri. The center of the area (Algaili town) is located 50km North of Khartoum city.
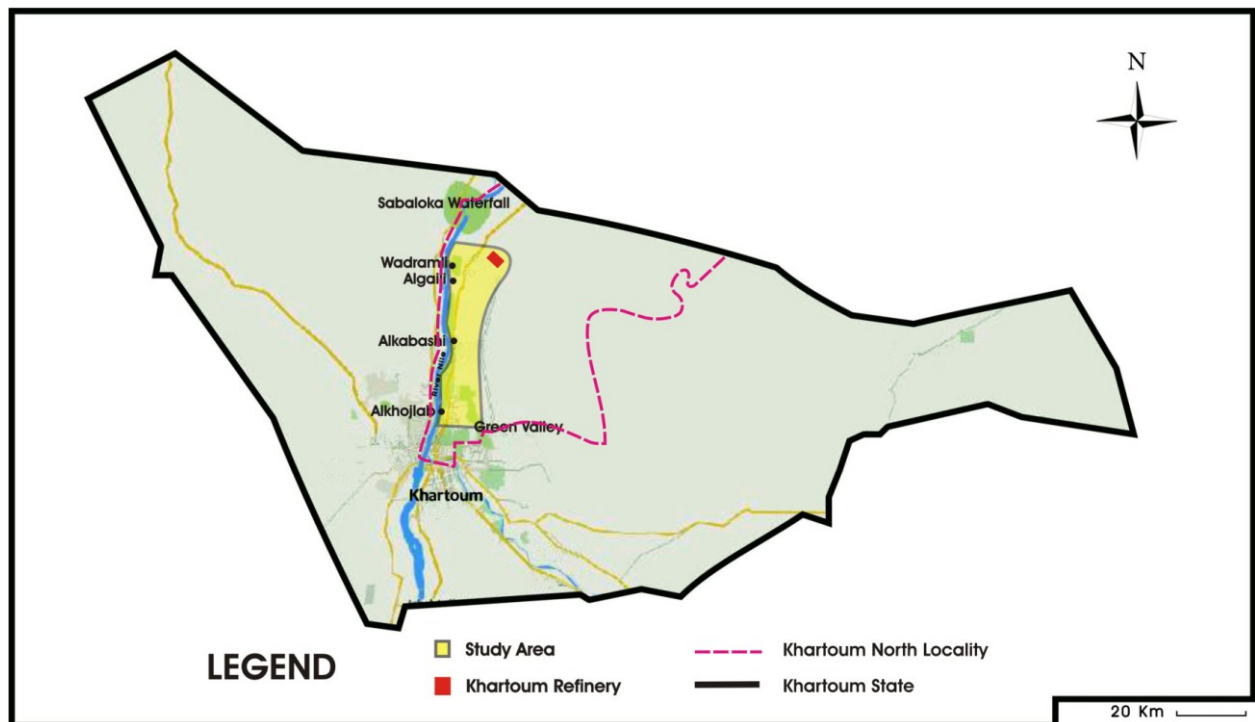
**Figure 1.4 :** The map of Khartoum State showing the study area.

Source: Google Maps Website- Modified.

Khartoum Refinery (Lattitude: 16.12952 and Longitude: 32.6881), Average elevation 412 meters (1,352 feet) is 65km North of Khartoum city, and surrounded by many environmentally sensitive sites. It is 13 km East of the River Nile, about 17km North-East of Algaili Town and Elnaia, Aldawm , and Wawissi villages, and 10km East of Wadramli and other villages in the neighbourhood (Figure 1.5). Also large landfill site owned by the Refinery is located 12 km East of it. This landfill site receive various hazardous wastes from the refinery.

**Figure1.5** : Satellite view of the Site and external neighbourhood of Khartoum Refinery. Source: Google Earth Website- Modified

## 1.12.1 Climate

The region have semi-desert climate with low rainfall rate. The weather is rainy in the summer, and cold and dry in the winter. Average rainfall reaches 100–200 mm in the northeastern areas and 200–300 mm in the northwestern areas. The temperature in summer ranges from 25 to 45°C from April to June, and from 20 to 35° C in the months of July to October. In winter, the temperature declines gradually from 25 to 15° C between March and November.

## 1.12.2 Population and economy

According to the 2008 Census figures **(CBS, 2009)**, Khartoum North locality area has a population of 608,817. Algaili region, the study area, has a population of 69,377 as reported in 2008 cesus. In this rural area most people are engaged in agriculture , grazing, and poultry farms; therefore supply the capital, Khartoum,

with vegetables, fruits, dairy products, and poultry eggs and meat. There are also some residents living on the banks of the River Nile engaged in the trades dependent on the River Nile, such as pottery, brick-making, and fishing.

### 1.12.3 General geology

The site area lies within the Sabaloka complex which comprises an inlier of Precambrian Paleozoic crystalline rocks surrounded by cretaceous sedimentary sandstone locally known as Nubian Sandstone. Three rock types covering the area are Gneiss, Granite, and Amphipolite. The origin of the soil is hillwash deposits of different grain size ranging from gravel to clay with almost depth 0.50 m **(SGRA, 1997).**

### 1.12.4 Geomorphology

Sudan Geological Research Authority (SGRA) **(1998)**, studied the geomorphological and geotechnical maping of the study area . The findings are summarized below.

### 1.12.4.1 Topography

The area is generally flat containing a number of isolated hills, rocky exposures, and soil cover. The whole area is gently dipping westward with a number of shallow, dry wadis draining through the area from high ridges in the east towards the River Nile in the western part.

### 1.12.4.2 Drainage pattern

The study area is characterized byt wo types of drainage patterns :

(a) Radial pattern : Represent the drainage patterns around the high terrains. They are controlling the draining in the watershed area and in some parts of the Nile terraces.

(b) Dendritic pattern : They are the most common patterns in the study area. They found in a form of long shallow wadis through which the area drams during the rainy seasons.

**1.12.4.3 Terrain units**

The study area is divided into four terrain units on the bases of the relief and topography as follows :

(a) Flat and gently dipping terrain: This unit is the dominant one in the study area. It represents the lowest parts in the area and covered mainly by colluvial and flood plain deposits.

(b) Low hills unit: It consist of the low hills and rocks exposures scattering in the area composed mainly of Gneiss . These hills have moderately- gentle slopes.

(c) Moderately high hills: This unit consists of very limited number of steep isolated hills. They composed of gray and migmatized Gneiss. J.Melaket represent the highest crust in the study area (approx. 50m).

(d) Structural ridge: It is an elongated ridge occupying the eastern part of the area. This ridge is trending  approximately North-East and acting as a water divider. It composed of sandstone, Conglomerate and sediments cover. Sheet erosion is common in this unit.

**1.12.4.4 Geomorphologic processes**

The main geomorphologic procsses acting in this area are weathering, erosion, and mass movement.

# Chapter Two
# Literature Review

## 2.1 Crude Oil Composition

Crude oils are a naturally occurring complex mixtures of tens of thousands of different hydrocarbon molecules, and small amounts of other non- hydrocarbons and mineral impurities. crude oils range in consistency from water to tar-libe solids and in color from clear to black. Some light crudes have specific gravities as low as 0.85, while others have specific gravities up to 1.15 **(Veenstra and Mohr, 2000)**. Although the proportions of the elements in crude oils vary over fairly narrow limits, a wide variation in properties is found from the lightest crude oils to the highly asphaltenic crudes. At the elemental level, oil consists of elements such as carbon 84-87%, hydrogen 11-14%, nitrogen 0.1-2% oxygen 0.1-2%, sulfer 1-3% and less than 1% each of metals and salts **(Simanjenkov and Simanzhenkov, 2003; McKetta, 1998; Mc Cain, 1990)**. Crude in the standard production and transpiration method, is inevitably associated with dissolved water and salts. The physical characteristics and chemical composition of crude oil and the yields and properties of products or fractions prepared from it vary considerably and depend on the concentration of the various types of hydrocarbos as well as on the amount of heteroatoms (nitrogen, oxygen, sulphur, and metals) in it **(Speight and Ozum, 2002)**. The concentration of these constituents in crude oils varies according to its source and dictates their marketability. Of the crude oil constituents, 98% are organic **(Wright and Welbourn, 2002)**.

Due to the complex composition of crude oils, characterization by the individual molecular types is not possible, and elemental analysis is unattractive because it gives only limited information about the constitution of petroleum due to the constancy of elemental composition. Instead, hydrocarbon group type analysis is commonly employed. Knowledge of the distribution of major structural classes of

hydrocarbons in crude oils is needed in various fields in the petroleum industry. Examples are studies related to reservoir evaluation, migration and maturity, degradation processes, processing, and environmental effects. The environmental impacts of the wastes generated in the petroleum refinery depend on amount and nature of pollutants released, which, intern depend, to a great extent, on the composition of the crude oil processed.

**1.Hydrocarbons**

Hydrocarbons constitute over 70% of the crude oil, and there are two things that make them exciting to chemists:

(a)Hydrocarbons contain a lot of energy and many of crude oil derivatives, like fuel, take advantage of this energy.

(b)Hydrocarbons can take on many different forms.

In crude petroleum, the hydrocarbon groups of interest include:

(a)normal paraffins: straight chain alkanes.

(b)Isoparaffins : branched chain alkanes.

(c)Naphthenes: cycloalkanes.

(d)Aromatics: unsaturated ring- based compound.

(e)Resins: large- chain, pyride.

(f)Asphaltenes: high molecular weight (300+) condensed aromatics. Another hydrocarbons like, alkenes, alkynes and dienes are found in crude oils.

The SARA- separation is a group type analysis, separating the crude oils in four main chemical classes based on differences in solutbility and polarity. The four SARA- fractions are the saturates (S), aromatics (A), resins (R) and the asphaltenes (A). More comprehensive crude assays determine the value of the crude (i.e. its yield and quality of useful products) and processing parameters. Crude oils are usually grouped according to yield structure. They are also defined in terms of API (American Petroleum Institute) gravity. The higher the API gravity, the lighter the crude and the lower the specific gravity.

## 2.Non-hydrocarbons

The non-hydrocarbon constituents of crude oil may be considered to fall into two categories **(Valkovic, 1978)**. A number of organic or metallo- organic compounds are more pr less indigenous to crude oil and are found in all crudes to some degree, regardless of source. These include: various oxygen containing materials, sulfur compounds and nitrogenous matter. Metallo-organics present initially or formed by interaction with surounding mineral material include chelate compounds metal soaps and possibly oil- soluble metal alkyls. The second group of non-hydrocarbons conists of impurities or contaminants whose presence is not directly related to the gensis of the crude oil. These are primarily colloidal or suspend entrained inorganic materials and emulsified water containing dissoved salts. The occurence of small amounts of metals has been reported also. In general sulfur, vanadiun, nickel, and nitrogen in the crude are associated with the higher-boiling material; they hardly appear in the light and middle distillates but are concentrated in heavier products.

### (a)Sulfur compounds

Sulfur may be present in crude oil as hydrogen sulfide ,as compounds (i.e. mercaptans, sulfides, disulfides and thiophenes) or as elemental sulfur which can also be present dissolved in the oil, possibly formed by the oxidation of hydrogen sulfide **(Hobson and Phol, 1973 )**. Each crude oil has different amounts and types of sulfur compounds, but as a rule, the proportion, stability and complexity of the compounds are greater in heavier crude oil fractions. Hydrogen sulfide is a primary contributor to corrosion in refinery processing units. Other corrosive substances are elemental sulfur and mercaptans. Moreover the corrosive sulfur compounds have an obnoxious odour. Crude oil that contain appreciable quantites of hydrogen sulfide or other reactive sulfur compounds are called "Sour" and those with less sulfur are called "Sweet".

**(b)Oxygen compounds**

Oxygen compounds such as phenols, ketones and carboxylic occur in crude oils in varying amounts.

**(c)Nitrogen compounds**

Nitrogen is found in lighter fractions of crude oil as basic compounds such as pyridine and quinoline and more often in heavier fractions of crude oil as nonbasic compounds (e.g. indoles, carbazoles and pyroles) that may also include trace metals such as copper, vanadium and / or nickel. Nitrogen oxides can form in process furnaces. The decomposition of nitrogen compounds in catalytic cracking and hydrocracking processes forms ammonia and cyanides that can cause corrosion.

**(d)Naphthenic acids**

Some crude oils contain naphthenic (organic) acids which may become corrosive at temperatures above 450 °F when the acid value of the crude is above a certain level.

**(e)Carbon dioxide**

Carbon dioxide may result from the decomposition of bicarbonates present in or added to crude, or from steam used in the distillation process.

**(f)Mineral impurities**

Mineral impurities in crude oil include:

I.Mechanical admixtures comprising particles of sand, clay and debris.

II.Water which is contained in crude oil in two forms; water which can be separated from oil by settling and water in the form of stable emulsions which can only be separated by physico-chemical methods.

III.Salts: crude oils often contain inorganic salts such as sodium chloride, calcium chloride and magnesium chloride in suspension or dissolved in entrained water (brine). These salts must be removed or neutralized before processing to prevent catalyst poisoning, equipment corrosion and fouling. Salt corrosion is caused by the hydrolysis of some metal chlorides to hydrogen chloride and the subsequent

formation of hydrochloric acid when crude is heated. Hydrogen chloride may also combine with ammonia to form ammonium chloride, which causes fouling and corrosion.

IV.Metals: metals including vanadium, nickel, iron, copper and zinc are often found in crude oils in samll, but measurable quantities. Because of their relative abundance in crude oils and asphalts, vanadium and nickel of naturally occuring hydrocarbons have been the most frequently studied metals **(Valkovic, 1978)**. According to Yen **(1975)**, the metallic components in petroleum can be classified into the following components:

- Metallo porphyrin chelates (V/Ni).
- Transition metal complexes of tetradentate mixed ligands such as V, Ni, Fe, Cu, Co, and Cr.
- Organometallic compounds such as Hg, Sb, As.
- Carboxylic acid salts of the polar function groups of resins such as Mo, Zn, and Ge.
- Colloidal minerals such as silica and NaCl.

**2.2 Petroleum Refinery Operations**

Ptroleum refineries are a complex system of multiple operations **(**Figure 2.1**)**. The operations used at a given refinery depend upon the properties of the crude oil to be refined and the desired products. For these reasons, no two refineries are alike. Portions of the outputs from some processes are refed back into the same process, fed to new processes, fed back to a previous process, or blended with other outputs to form finished products **(US EPA, 1995)**.

Refinery operations are divided into four basic categories: fuel production; by-product processing; ancillary operations and wastewater management. Fuel production encompasses those operations which manufacture petroleum products such as gasoline and coke. By-product processing covers refinery operations that convert used materials and/or undesirable petroleum constituents into salable or

reusable end products. Ancillary operations recover energy. Finally, wastewater management deals with the treatment of refinery wastewaters including the recovery of usable oil products from refinery wastewater streams.

## 1.Petroleum product production

There are three basic raw materials used in the crude oil refining process : crude oil; catalysts; and process chemicals. Heat, the final component in this process, is used to accelerate reactions, separate components, and reduce viscosity. Crude oil arrives at the refinery by ship or pipeline and is stored in tankage prior to processing. Initial separation of crude components occurs in distillation columns. Subsequently, materials recovered by distillation are used as a fuel source in the refinery, or sent to other processes to generate useful products. According to California Environmental Protection Agency **(1997)**, the processes used to produce salable petroleum products are :

## (a)Distillation

Distillation is the first process a barrel of crude oil encounters after it leaves the crude oil storage tanks in the refinery. Crude oil consists of many miscible substances all with different boiling points. While it is virtually impossible to separate each compound in crude oil individually, the distillation process uses temperature and pressure control to effectively separate groups of compounds with similar boiling points into unique mixtures.

Crude oil is initially heated and salts are removed prior to distillation. The first material to separate out from the crude oil mixture during distillation is the sour (hydrogen sulfide containing) gases. Sour gases are routed to refinery plants so that hydrogen sulfide can be separated from fuel gases. Hydrogen sulfide does not have value as a fuel source but is an important source of sulfur which can be recovered for use in the refinery or for resale to other industries. The next fraction removed during distillation are propane and butane. These materials can be processed further and sold as liquefied petroleum gas (LPG) , used as an in-plant fuel source or used

to produce hydrogen or other chemicals. Continues fractionation in the distillation columns yields gasoline, jet and diesel fuels. The lower boiling materials, gas oil and reduced crude, are the last materials to separate and require additional processing to reach desired endpoints. Reduced crude is used as feed materials in vacuum distillation columns (distillation under vacuum lowers the boiling point of the materials and eases separation).

**(b)Hydrotreating**

Hydrotreating is a catalytic process which uses hydrogen to improve the stability of and remove impurities from distillation products. Impurities in crude oil such as sulfur, nitrogen and metals must be removed to meet product specifications and to prevent poisoning of catalysts used in some down stream processes. A potential negative side effect of hydrotreating is hydrocracking. During hydrocraking desirable hydrocarbons are broken up into potentially unusable by-products.

**(c)Catalytic reforming**

Catalytic reforming employs catalysts to mediate reactions that boots the octane level of distillation products. During the process of catalytic reforming, hydrogen is produced for use in hydrotreating. Catalytic reforming encompasses four types of reactions:

I.Dehydrogenation of naphthene to produce aromatics.

II.Dehyrocyclization of paraffins to naphthenes and aromatics.

III.Isomerization of naphthenes and paraffins to more highly branched isomers.

IV.Cracking of naphthenes and paraffins to shorter hydrocarbon chains.

The fourth reaction listed above is undesirable because it reduces yields, lowers hydrogen purity and consumes hydrogen.

**(d)Hydrocarbon cracking**

Hydrocarbon cracking is a process in which large molecules are cleaved into smaller ones. This process can be accomplished either thermally or catalytically resulting in maximization of salable products from crude oil. During catalytic cracking of hydrocarbons, the catalysts act to increase the yield of desirable

products and minimize the production of less useful materials, or allow cracking to occur at more favorable temperatures and pressures.

Thermal cracking, which occurs in the coker, is a process that is typically used to crack the heaviest hydrocarbons, the residuum. Coke, a hydrogen poor (carbon rich) by-product of thermal cracking is left over after heating, is also sold as a fuel source.

## 2.By-product processing

During the petroleum product refining process, by-products are produced that have resale value or they may be reused directly in refinery processes thus displacing normal feed stocks. Some of these by-products, such as hydrogen sulfide which is used in sulfur production, are natural constituents in crude oil that are removed to make the products cleaner.

## (a)Sour water/gas processing

One of the principal by-products of petroleum refining is sour off-gases. Sour gases contain hydrogen sulfide, a noxious volatile compound, that easily stripped from crude oil or partially refined products containing hydrogen sulfide and may be transported to hydrogen sulfide ($H_2S$) plants. The hydrogen sulfide plants effectively separate sour off-gases into "sweet" and "sour" fractions. "Sweet" gases containing low hydrogen sulfide levels are then transported to the refinery fuel gas system while sour gases are routed to Claus sulfur units for sulfur recovery (sometimes referred to as the Stretford Process). The Claus units produce elemental sulfur.

Sour waters are also generated by many processes at the refinery. In addition to hydrogen sulfide, ammonia is also present in sour waters. Sour water is first concentrated in stripping towers and subsequently delivered to facilities capable of recovering the ammonia. During ammonia recovery, hydrogen sulfide is separated out and returned to the sulfur recovery process.

**(b)Caustic and acid**

A critical chemical used in the oil refining process is caustic soda. After being used in the production of jet fuel and light gasoline, the caustic soda, with entrained cresols or naphthenes, is sold as a product. After leaving the refinery, these materials are processed to create fresh caustic soda and to recover the cresols and naphthene. Spent sulfuric acid, used in alkylation and also to treat jet fuels, remains sufficiently concentrated, and it is sold typically for off-site remanufacture as commercial acid.

**3. Ancillary operations**

Ancillary refinery operations include power production and process water purification. These operations do not directly result in a salable product; however, they are desirable operations because they reduce costs, recover energy (power production), and provide softened water for refinery processes.

**(a)Cogeneration**

In the Cogeneration (Cogen) Plant refinery fuel gas, natural gas, and LPG are used to generate electricity from turbines located on site and to fire boilers that produce steam. Steam is a critical in many refining processes and for the generation of electicity.

**(b)Water treatment**

The water treatment system consists of the demineralizing and softening municipal drinking water prior to use in refinery operations. Inorganic ions such as sodium, calcium, magnesium, and chloride are removed from drinking water using exchange resins. The purified water created in this process extends the life of refinery equipment by reducing scale and eliminating compounds which interfere with the refinery processes.
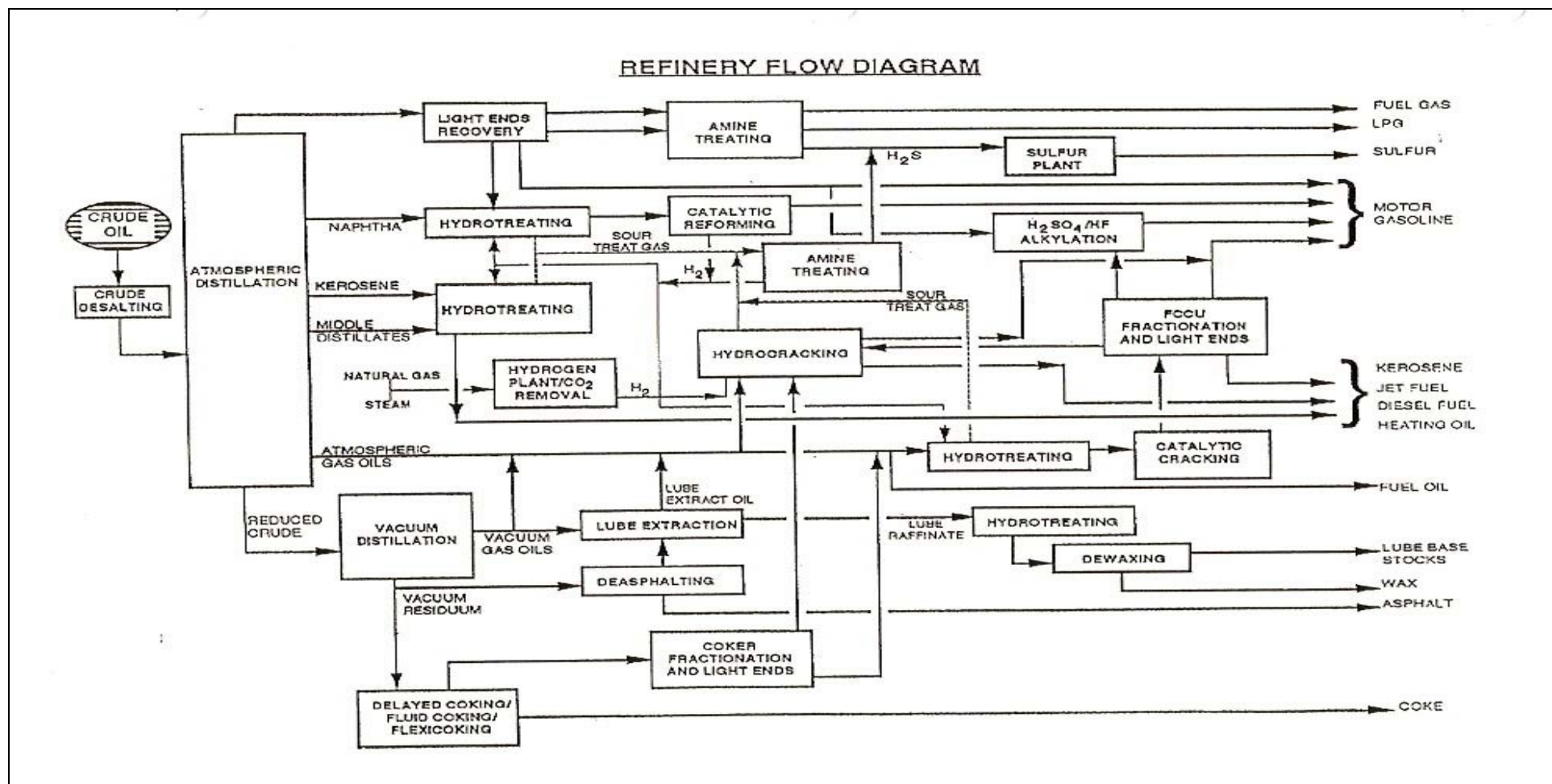
**Figure 2.1**: Typical refinery flow diagram. Source: Haydel (2003). Petroleum Refinery Processing.
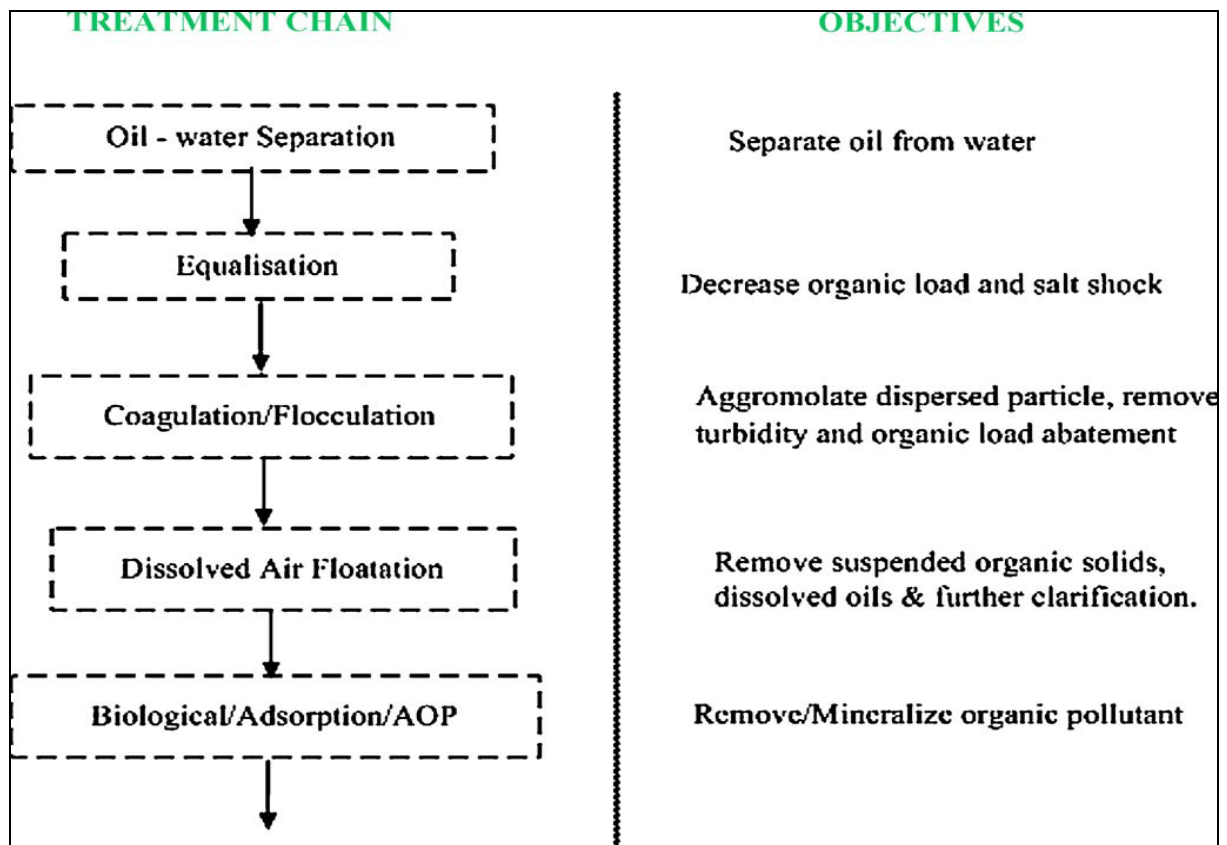
## 4.Wastewater management

Wastewater treatment includes mechanical, physicochemical, and biological purification of aqueous wastes (Figure 2.2). Part of this process involves oil/water separation. This leads directly to the recovery of oil and oil products from the refinery effluent system. Wastewater treatment facilities consist of both passive and active oil/solids separation, oil recovery, biological wastewater treatment, and biological sludge digestion. The collection of wastewater is accomplished using a parallel system of pipes designed to carry different wastewater materials. This two tiered wastewater collection system is referred to as the segregated and unsegregated drain system. The segregated drainage system collects discharges from refinery operations producing process wastewaters. The unsegregated system is used to convey non-process wastewaters, such as cooling tower blow down, and rainwater runoff. The parallel system join after passing through their respective treatment facilities and ultimately discharged.

Passive oil/solids separation is a process common to both the segregated and unsegregated systems. Separation is accomplished by transmitting wastewaters through an oil/solids separator where materials are removed from the water based on their differing densities. Oils, which float on water, are recovered from this process and the settleable solids are periodically removed from the separator bottom. Active oil separation processes are employed on both the segregated and unsegregated systems. These processes include dissolved and induced air flotation (DAF and IAF respectively) units. Oil removal by the DAF unit occurs down stream of passive oil separation in the segregated system. An IAF is used to polish unsegregated system flow, including runoff.

The biological wastewater treatment plant takes all wastewater flow from the segregated drainage system. This facility consists of an activated sludge process for the removal of dissolved organic material. Subsequent to biological processing,

**TREATMENT CHAIN**

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│  Oil - water Separation │
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            ▼
  ┌───────────────────┐
  │   Equalisation    │
  └───────────────────┘
            │
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┌─────────────────────────┐
│ Coagulation/Flocculation│
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  ┌───────────────────────┐
  │ Dissolved Air Floatation│
  └───────────────────────┘
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│ Biological/Adsorption/AOP│
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            │
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**OBJECTIVES**

Separate oil from water

Decrease organic load and salt shock

Aggromolate dispersed particle, remove turbidity and organic load abatement

Remove suspended organic solids, dissolved oils & further clarification.

Remove/Mineralize organic pollutant

**Figure 2.2** : Schematic diagram of generic sequence for treating petroleum refinery effluent. Source: Diya'Udeen et al., (2011).

solids generated during biological treatment are removed by settling in clarifiers. The majority of the settled material, which consists of biological matter, is recirculated to the process to maintain aerobic (oxygenated) biological treatment activity. The balance of this separated biological solid is processed in the sludge digester. Sludge digestion is an anaerobic process (biological treatment occurs without oxygen) that reduce the mass of biological solids. Digested sludge is ultimately disposed of to the sanitary sewer or sent for dewatering and disposal to drying beds or by other means.

Throughout the wastewater treatment process, oil recovery is a preference to extract usable crude oil and refined or partially refined petroleum products from liquid material are transported to tanks and allowed to passively separate.

Recoverable oil is removed after passive separation and returned to the refining process. Solid and semi-solid secondary materials generated in the wastewater treatment process are processed to recover trapped oil via Mobil oily sludge coking (MOSC) or another alternative such as mechanical separation.

## 2.3 Petroleum Refinery Liquid Effluents

The petroleum industry uses very large quantities of water. The principal use of water by the industry is in the refining branch. Other operations such as the transportation of crude oil and products and marketing do not use significant amount of water. Some water is used in the producing branch for drilling wells and operation of natural gas plants, but the amount is small in relation to that used in refineries.

Large amounts of water are used in a petroleum refinery and, consequently, significant volumes of wastewater are generated (0.4 – 1.6 times the volume of processed oil), **(Parilti, 2010)**. The water demand for refineries is up to $3m^3$ of water for every ton of petroleum processed **(US EPA, 1980; US EPA, 1982; WB, 1998)**. The refinery consumes approximately 65 to 90 gallons of water for every barrel of crude petroleum it refines

Almost 56% of this quantity is used in cooling systems, 16% in boiling systems, 19% in production processes and the rest in auxiliary operations. The water supply and the distribution for the different uses depend on the oil transformation processes in the refinery, which are based on the type of crude petroleum that the refinery processes and on the generated products. The quantity of the wastewater generated in the refineries is almost 50% of the used fresh water, **(WB, 1998)** , **(US EPA, 1982)** . European refineries (range from 0.5 to more than 20 million tonnes), generate, per million tonnes of crude oil refined, from 0.1 – 5 million tonnes of wastewater, **(EU Commission, 2003)**. However, Wastewaters generated by oil refining plants have variable composition, depending on the units in operation and

type of oil processed **(Wake, 2005)**. Different collection systems are used in the refineries, depending on the effluent composition and the point of generation. The main water sources of water used in petroleum refineries are surface water, groundwater, and desalinated water.

Wastewater in oil refineries originates from several sources and varies according to the quantity and degree of contamination. The wastewater contains oil, the major contaminant in the wastewater being composed of a range of different hydrocarbons and other organic compounds present in the crude oil and chemical substances produced by the refinery process such as sulphides, mercaptans, cyanides, ammonia, phenols, inorganic salts, and traces of some heavy metals. Other contaminants that are not generated in the petroleum refining operations but also can be present in the wastewater include additives used for blending, conditioning agents for raising steam and cooling water, and products used in the control of equipment corrosion.

The major water flow contributions to the wastewater treatment plant units within oil refineries may arise from the following sources **(de Brito, 2009)**.

### 2.4.1 Ballast water

Ballast water from ships and product tankers, arriving at the refinery in ballast. Ballast water may represent a significant contribution for a coastal/estuarine refinery and may indeed have to be handled as a separate facility.

### 2.4.2 Process water

Water originating from the process units such as: drainage of the bottom of crude and product tanks, crude oil washing, oily condensates from steam stripping, steam products from the distillation and chemical conversion units, and sour waters.

### 2.4.3 Cooling water

Cooling water is not normally contaminated with oil, except in the event of heat exchanger tube failure. However, the wastewater of a cooling tower may contain low concentrations of conditioning chemicals.

### 2.4.4 Stormwater

Rain water run-off from paved areas in the processing units or the product loading stations, due to small spillages;

### 2.4.5 Sanitary sewage

This is the wastewater coming from the living area and offices.

Therefore the performance and degree of complexity of the wastewater treatment plant designed to treat refinery wastewaters will depend on the quantity and the degree of contamination of the wastewater, and even on the location of the discharge, that is, whether it is to a river, estuary or the sea.

Sour waters in particular represent the worst source of chemical contamination to the wastewater, and in most cases they are separated from the other sources of water and their release into the biological unit are controlled by dilution. Sour waters are the by-product of conversion processes such as cracking and hydrogen treatment of oils containing significant amounts of sulphur and nitrogen compounds, one part of which ends up as hydrogen sulphide and ammonia, and the other part of which leaves the plant as a water solution. Sour waters also may contain variable amounts of oil (in dissolved, suspended or emulsified state) dissolved inorganic salts and dissolved organic compounds, such as light hydrocarbons, phenols, thiophenols and other oxygenated products like organic acids. A significant amount of the wastewater is contributed by the desalters, vessels in which oil coming from the field is washed, in order to remove dispersed inorganic salts.

## 2.4 Environmental Impact of Refinery Effluents

Oil refinery effluents contain many different chemicals at different concentrations. The exact composition cannot however be generalised as it depends on the refinery and which units are in operation at any specific time. It is therefore difficult to predict what effects the effluent may have on the environment. The overall treated wastewater from the water treatment plant and the volume coming from the untreated oily sewer pond are discharged into the near environment. The total quantity of aqueous effluent that is being discharged by oil refineries has decreased over the years, for example European refineries discharged $3119 \times 106$ t year -1 from 80 refineries in 1969 reducing to $2543 \times 106$ t year -1 from 84 refineries in 2000. The decrease between 1974 and 1978 is thought to be due to more refineries using air cooling and recirculating cooling water systems, **(Concawe, 2004)**. Over the years the complexity of refineries has increased and since 1969 there has been the introduction of more effective treatment systems. The three main treatment processes for effluent before its discharge are gravity separation (API separators, tank separation), advanced treatment (flocculation, sedimentation, filtration) and biological treatment (biofilters, activated sludge, aerated ponds), **(Concawe, 2004)**. The percentage of refineries that have all three treatment processes has increased over the years as not all refineries have the same processes, but the effluents that are produced will have different chemical compositions depending on the type of treatment they receive **(Nnabugwu, 2013)**. Wastewater released by crude oil refineries are characterized by the presence of large quantities of crude oil products, polycyclic and aromatic hydrocarbons, phenols, sulphides, cyanides, suspended solids, nitrogen compounds as well as heavy metals such as iron, nickel, selenium, copper, zinc, and molybdenum **(Zhu *et al*., 2001; Chikere and Okpokwashi, 2004; Kuehn *et al*., 1995; Nwanyanwu and Abu, 2010)**. It has been well established that the hydrocarbon components of petroleum are composed of paraffinic, naphthenic, and aromatic groups, besides non- hydrocarbons (sulphur compounds, nitrogen-oxygen compounds and heavy metals) **(Speight, 2006)**.

Refinery effluents tend to have fewer of the lighter hydrocarbons than crude oil but more polycyclic aromatics which tend to be more toxic and more persistent in the environment **(Wake, 2005)**.

If liquid hydrocarbons are released to groundwater and surface waters, migration off-site can occur resulting in continuous seeps to surface waters. While the actual volume of hydrocarbons released in such a manner are relatively small, there is the potential to contaminate large volumes of groundwater and surface water possibly posing a substantial risk to human health and the environment. However, due to the ineffectiveness of treatment systems, wastewaters may become seriously dangerous, leading to the accumulation of toxic substances in the receiving environments with potentially serious consequences on the ecosystem **(Chikere and Okpokwashi, 2004)**. Therefore, discharge of these effluents containing persistent chemicals may result in long term effects in aquatic and terristrial environments. Many researchers studied pollutants discharge by petroleum refineries. For instance, Elhaj **(1985),** reported that the amount of oil and greases discharged into the Red Sea from portsudan refinery, Portsudan, Sudan, represents 17% of the total oil discharged by the industrial sector. **Bekheit (1995),** stated that the mean concentration values for oil content and suspended solids of the combined effluent, in Port Sudan refinery, were found to be 87.2 mg/l and 1090.6 mg/l respectively, which were higher than the permissible limits stated in the operating agreement. However, the fate and effects of oil refinery effluent once it is discharged into the environment depends on the conditions of  the receiving environment. According to Wake **(2005)**, The area around the discharge is often found to have a low diversity and abundance of fauna due to the inability of many species to survive in such close proximity to the effluent, and in some cases the area adjacent to the outfall can be completely absent of any fauna, such as in the Hooghly Estuary, India, where no bottom fauna was found around the refinery outfall. Effects on the flora have also been seen. In the Medway Estuary  and

Milford Haven (both in UK), algal growth has been seen to increase near the effluent, algae are notably abundant around the outfalls in these areas **(Wake, 2005)**. Effects of refinery effluents on invertebrates and fish were investigated by many researchers **(Stuart, 1979)**, **(US EPA, 1976)**, respectively.

Refinery effluents when discharged directly into the rivers without prior treatment have capacity of increasing water quality parameters. The resultant effects of this will be on the receiving streams and rivers. The impacts could include water quality impairment, reduction in fish abundance and effect on water-usage for recreation, industrial and domestic purposes. Otokunefor and Obiukwu **(2005)**, Nwaichi et al., **(2013)**, Lekwot et al., **(2012)**, Nnabugwu **(2013)**, and Sarkodie et al., **(2014)**, have all shown that the pollution levels of aquatic ecosystems observed in the recipients are a result of unregulated effluent discharges from petroleum refineries.

Pollution of soil ecosystem is the introduction of excessive amount of substances which alters the properties of the soil from its original state or interfere with the legitimate use of the soil environment. Pollution of the soil ecosystem is a major source of soil degradation **(Lekwot *et al*., 2014)**. Soil ecosystem is an essential component of life and man depends on it for food and natural resources while plants depend on it for their growth. It is also a medium for the biochemical cycling of soil nutrients. So, as the soil is being contaminated with all manner of pollutants, the life process is being disturbed and hence there may be imbalance in the whole system. it has been shown by Lekwot et al., **(2014)** that, emissions from Kaduna refinery plant and the petrochemical complex have devastating effects on soil fertility. Konwar and Jha **(2010)** and Roy **(2001)** observed negative influence of refinery effluents on the yield of rice.

## 2.5 Toxicity of Refinery Effluents

Toxicity tests have shown that most refinery effluents are toxic with positive correlations between pollution from refinery effluents and the health of aquatic organisms, but to varying extents and also organism specific. Previous observations **(Kuehn *et al*., 1995)**, suggested a correlation between contamination of water and sediments with aromatic hydrocarbons from refinery effluents, and compromised fish health. However, the toxicity of oil refinery effluent is dependent on a number of factors **(Thakur, 2006)** ; the volume, quality, salinity and variability of the discharge, the siting of the outfall, the physical and chemical conditions of the discharge area, the proximity of other effluents and pollutants and the biological condition of the discharge area. Daflon et al., **(2015)** Who evaluated the cause of the chronic toxicity of a refinery wastewater from Brazil using the organism Ceriodaphnia dubia in short-term test, reported that although the physical and chemical levels of in the effluent were below those established by the Brazilian regulation, they were not sufficient to prevent the chronic toxicity of the refinery's wastewater, and their results suggest that metals such as barium, manganese and strontium can be contributing for the toxicity of the wastewater, and besides this, conductivity could be contributing to the toxicity too.

The different components of the refinery effluent can have varying effects and toxicities. The oil in the refinery effluent can affect aquatic organisms in a number of different ways. It can kill them directly through coating and asphyxiation, contact poisoning, or through exposure to water-soluble components. It can also cause the destruction of more sensitive juveniles or of the food organisms therefore wiping out a population. Lastly oil is capable of causing sublethal and stress effects, carcinogenic and mutagenic effects and can effect the behaviour of individuals **(Wake, 2005)**. The toxicity of ammonia is dependent on pH, oxygen concentration and temperature. With increasing pH and decreasing $O_2$ ammonia becomes more toxic. Ammonia is removed by bacteria in well-oxygenated areas

and is therefore not likely to be accumulated by marine organisms **(Concawe, 1979)**. Sulphides on the other hand are also removed by bacteria **(Concawe, 1979)** but have the opposite relationship with pH. The toxicity of sulphides increases with decreasing pH. Cyanides are also very toxic to marine organisms and the toxicity is affected by synergism with other compounds like ammonia and zinc. Cyanide affects the transport of oxygen from the blood to the tissues. Phenols on the other hand are less toxic and are readily biodegraded by bacteria within 200 min given the right conditions **(Wake, 2005)**. Lastly heavy metals can have toxic effects. The different metals have varying effects that also vary with temperature, salinity, pH and valence and can act synergistically with one another **(Wake, 2005)**. The exact effects of refinery effluent and its constituents thus can and do vary between species and from location to location.

## Chapter Three
## Research Methodology

This chapter describes the research methods used to obtain and process data to allow an empirical research assessment to be made of Khartoum refinery liquid effluent.

### 3.1 Research Design

Two designs are carried out in this study which are survey research which involved the field survey, and one -to- one interview and experimental research which involved samples collection and laboratory analysis.

**Survey research;** which involves the collection of data through personal interviews and field survey by visiting in person the following sites:

• Most of the villages along the River Nile bank in the study area from Abohalima to Garri.

• Vegetables, fruits, grains, and poultry farms.

• Grazing areas.

• Wadis distributed in the area reflecting the drainage pattern.

• Water supply station of Khartoum Refinery at Dabak village on the River Nile bank.

• Khartoum Refinery, including all units and oxidation ponds site.

**Experimental research;** which involves sampling and laboratory analysis and investigation. Liquid effluent samples from both the monitoring pond and the oxidation ponds. Sediment samples were collected from oxidation ponds. Effluent and sediment samples analyses were carried out by competent laboratory scientists with actual participation of the researcher using appropriate referenced analytical methods.

## 3.2 Methods of Data Collection

For the purpose of this study, data was collected from both secondary and primary sources.

**Primary sources:** The primary source of data collection in this research is through laboratory analysis, one-to- one oral interview, field observations, and wastewater survey. First-hand information of the liquid effluents management was obtained from Environment manager and technicians of Water & Environment Laboratory. Engineers were interviewed to know current state of the WWTP and disposal of wastewater. This data were collected directly by the researcher. The data concentrated among other things, on the refining activities with emphasis on liquid effluent, its potential impacts on area environment, control strategies and management.

**Secondary sources:** Secondary data sources include published and unpublished materials. Published materials include books, and textbooks on petroleum composition and refining, World Bank and U.S EPA publications on environmental problems resulting from discharge of refinery effluents, journals from professional groups and other periodicals. Unpublished materials include documents and records from Geological Research Authority, Central Bureau of Statistics CBS, Meteorology Authority, Central Petroleum Laboratories CPL, and related dissertation works, lecture notes from institutions of learning, Conference papers, etc.

## 3.3 Sampling Sites

Two (2) main sample collection sites (Figure 3.1), were selected in the study area. These includes;

1. The wastewater monitoring pond (MP) : Located at the southwestern area of the refinery . This pond is the collection station of the whole refinery liquid effluent. Treated effluent reaches the monitoring pond after passing through the treatment system and before being discharged to the oxidation ponds outside the refinery in the surrounding area.

2. The oxidation ponds : In this location 3 positions were sampled namely;

➢ Pond A  ($P_A$) **(Figure 3.2)**

➢ Pond B  ($P_B$) **(Figure 3.2)**

➢ Pond C  ($P_C$) **(Figure 3.2)**
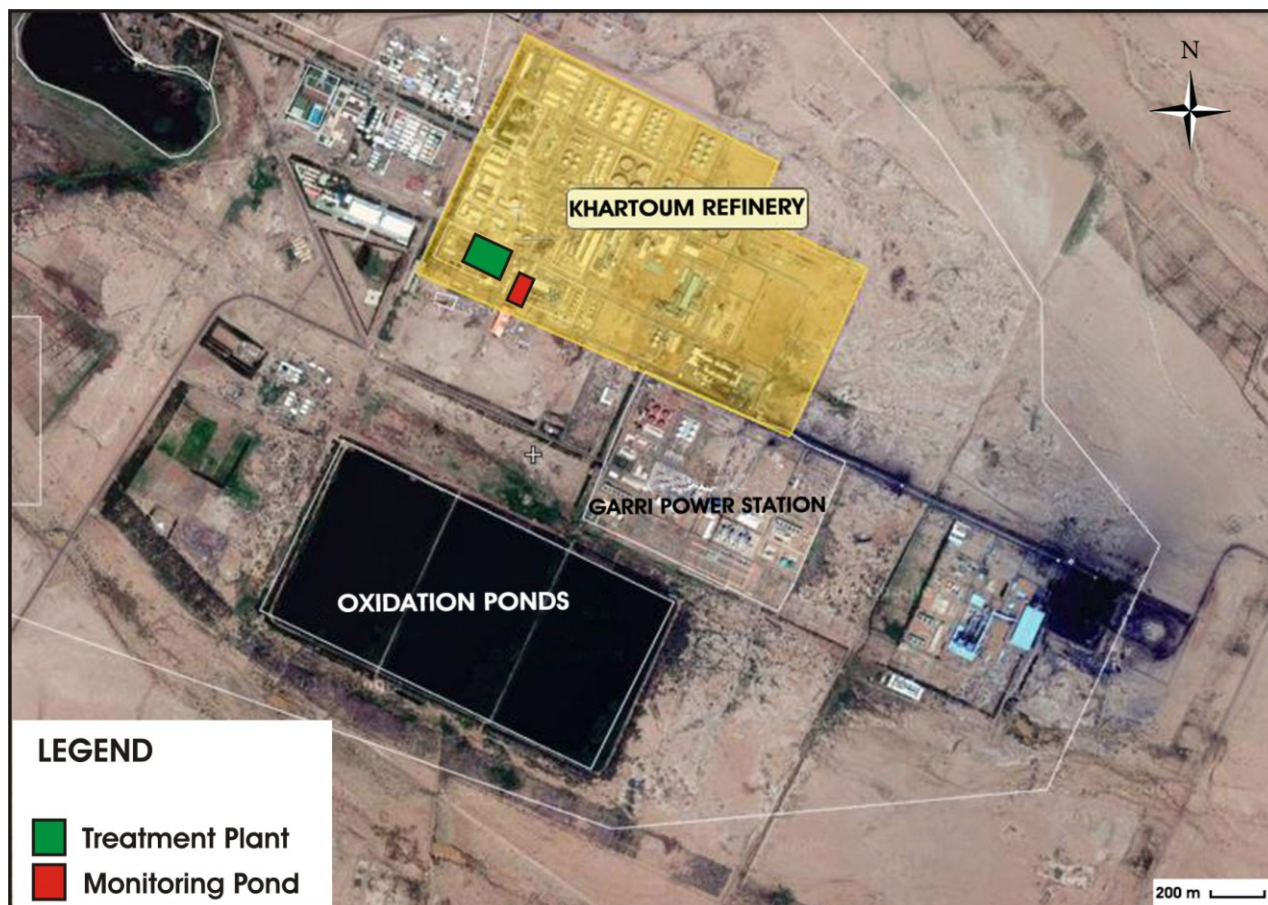


**Figure 3.1 :** Satellite view of Khartoum Refinery showing the main sampling sites; MP and the oxidation ponds. Also wastewater treatment plant (WWTP) can be seen. Source: Google Earth Website- Modified

The Oxidation ponds site is about 700 m south of the refinery. The ponds are arranged as pond(A), pond(B), and pond(C) from east to west. Each one is (1200×650) m, with water depth 3-4 m at the center. Each pond was sampled at 5 selected points **(Figure 3.2)**. These sampling points were:

1.   The center of the pond.

2.  The midpoint between the center and the north end of the pond.

3.  The midpoint between the center and the east end of the pond.

4.  The midpoint between the center and the western end of the pond.

5.  The midpoint between the center and the south end of the pond.
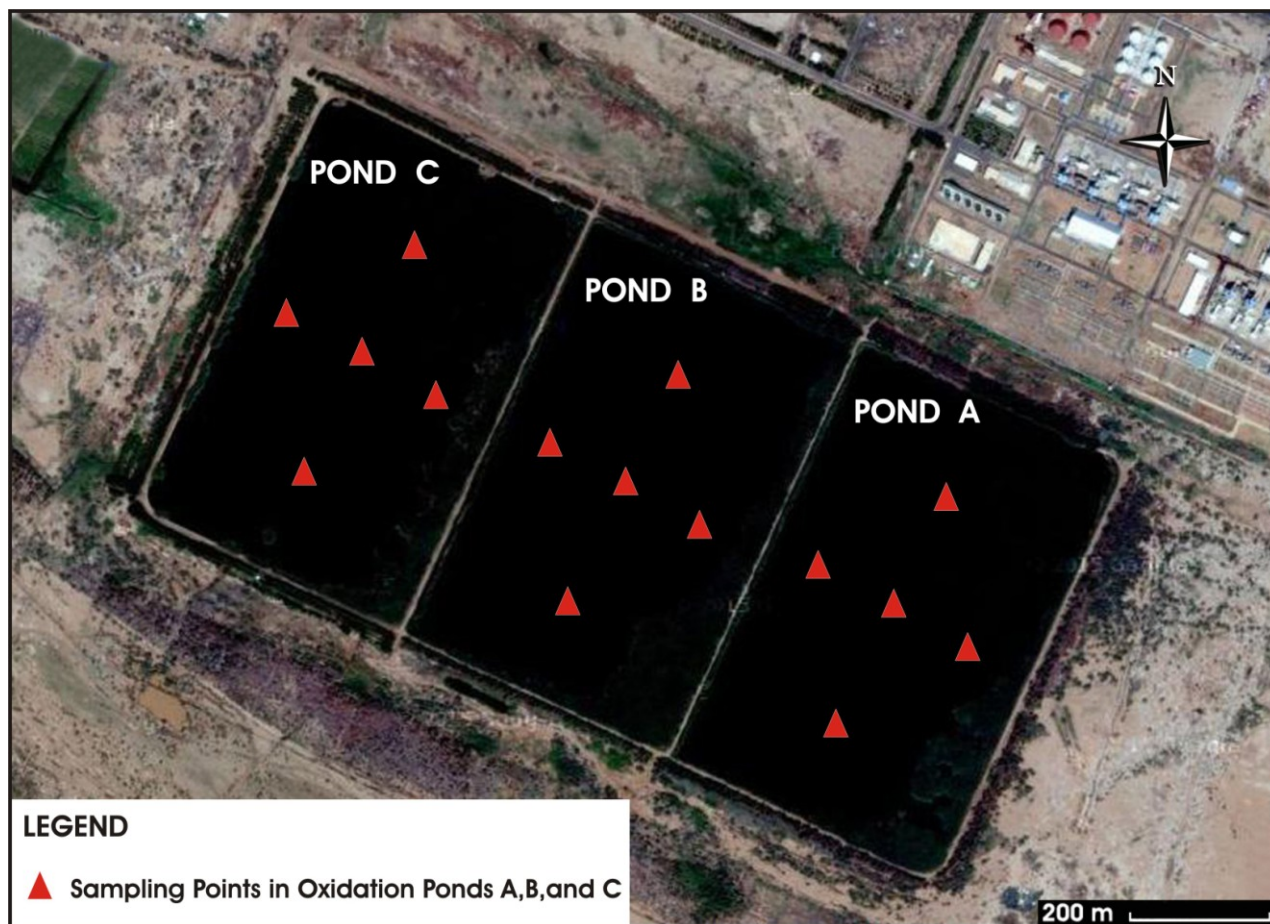


**Figure 3.2 :** Satellite view of the oxidation ponds showing pond (A), pond (B), pond (C), and sampling points in each pond. Source: Google Earth Website- Modified

## 3.4 Effluent Samples Collection and Pretreatment

Wastewater samples were collected from Khartoum refinery monitoring pond and oxidation ponds (pond (A), pond (B), and pond (C)), between February 2003 and April 2004, using a simple manual sampler made in a local private workshop especially to satisfy the collection of representative wastewater samples in the

present study. The sampler **(**Figure 3.3 **)** , has a hard cylindrical iron arm (4m long) and a valve- controlled iron cage for the glass sampling bottle.
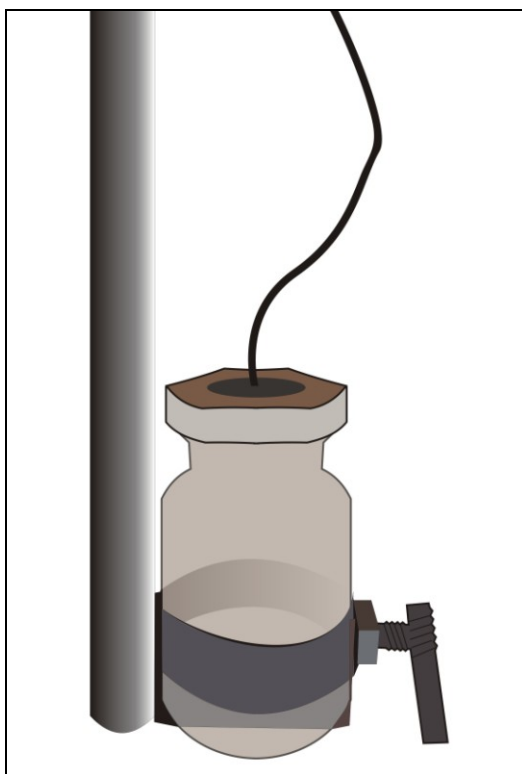


**Figure 3.3 :** Manual sampler used in effluent samples collection.

Monitoring pond (MP) effluent 9 composite samples were collected on february, 12-14, 2003 and each sample was a composite of 3 grab samples which were collected from three points below the surface ; the center and the north and south ends of the rectangular pond. For Turbidity, Hardness, Sulfide, Ammonia-Nitrogen ($NH_3$-N), Reactive Phosphorus (P-reactive), Total Phosphorus (P-total), Biochemical Oxygen Demand ($BOD_5$), Chemical Oxygen Demand (COD), Oil/Grease, and Phenols a composite sample for each day represents a combination of three grab samples collected on the basis of eight h intervals per day. Also a three-days composite samples were collected similarly for, Total Solids (TS), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), Electrical conductivity (Ec) , Alkalinity, Chloride, Sulfate, Cyanide, Nitrate-Nitrogen (NO3-N) , and

Nitrite-Nitrogen ($NO_2$-N) . The composite effluent samples collected throughout the three days were mixed together to give representative sample.

Oxidation ponds effluents were sampled between december, 2003 and april, 2004 utilizing an engine boat and with the aid of the same sampler as for monitoring pond effluent sampling. 27 composite samples of the effluent were collected from the oxidation ponds. Each sample was a composite of 15 grab subsamples from different depths and locations in each pond. The grab samples were gathered from three levels, (from surface, middle depth and bottom), at 5 sampling points ,(shown in section 3.3), after triple rinsing the appropriate container with the wastewater to be sampled. The grab samples were filled in intensively precleaned labled glass bottles  to make composite samples. Once collected, the samples were immediately preserved on site  according to the standard method of American Public Health Association **(APHA, 1998)**,  and kept in ice at a temperature of 4°C before being transported to the laboratory for analysis. Sampling equipments and samples containers were prepared and cleaned, according to "DECON" procedure **(Csuros, 1994)** , prior to samples collection. Chemicals and reagents used in samples preservation were of analytical reagent grade.

**3.5 Sediment Samples Collection and Pretreatment**

The bottom sediment samples were colleted by divers using a wide–mouth plastic bottles from a depth of about 0–10 cm. The samples were collected from Khrtoum refinery wastewater oxidation ponds between 16 and 24 April, 2004.

Five grab samples, (about 3kg total weight), were taken from each of the three ponds at the same wastewater sampling points (from the center and the midpoints between the center and the four ends of the pond). The grab samples of each pond were combined and mixed in prelabled polythylene bags $P_A$, $P_B$ and $P_c$ for pond (A), pond (B) and pond (C) respectively. After discarding stones and debris, the sediments were preserved by the addition of concentrated $H_2SO_4$(12.5 $cm^3$/kg), and

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kept in ice before being transported to the laboratory for analysis, to prevent microbial alteration of the sediment nature.

At the laboratory, sediment samples were homogenized and freez-dried for 36 h. Thereafter the quantity was reduced by quartering method and they were placed in polyethylene cups carefully covered with aluminum foil until further use. Higher heavy metal concentrations are generally found on smaller grains of sediment because of the higher surface area to grain- size ratio. There for, the smaller the grian size, the higher the metal concentration accumulation. As a consequence each sample was carefully grounded and mixed several times in a porcelain mortar and forced through a 45µm stainless steel mesh to restrict the grain size for more accurate results. Sampling bottels, sample containers and sieve meshes were cleaned by washing them with detergent, then soaked in 50% HCl and then rinsed with 1:1 $HNO_3$ and deionised water.

**3.6 Effluent Analysis**

Wastewater analyses were conducted by the central petroleum Laboratories (CPL), Sudanese Petroleum Corporation, Ministry of Energy& Mining, Khartoum, with the exception of few samples from MP wastewaters which were measured at Water and Environment Laboratory, Khartoum Petroleum Refinery itself.

For quality assurance all chemicals and reagents used were of analytical reagent grade or ACS. Contaminations were checked by running blanks and deionized distilled water was used through out the experiments. All glass apparatus and plastic containers were cleaned according to standard methods.

The collected samples were analyzed to measure the pollution parameters in wastewater, enabling assessment of the final treated effluent quality, and establishment of background base line data for pollution levels as well as allowing judging the compliance with the recommended limits, there for provide insight into

the potential of negative impact on the surrounding area and hence can assess the current environmental situation.

The wastewater samples were examined in accordance with the "Standard Methods for the Examination of Water and Wastewater", (**APHA, 1998**) , and the analyses were carried out for physical parameters (Temperature, pH, TS, TDS, TSS, Conductivity, and Turbidity), inorganics (Alkalinity, Hardness, Chloride, Sulfate, Cyanide, Sulfide and Hexavalent Chromium), nutrients (Ammonia-Nitrogen , Nitrate-Nitrogen , Nitrite-Nitrogen and Phosphorus), heavy metals (Cr, Cd, Ni, Fe, Pb, Zn, Ba, Ag, Se and Cu) and organics (BOD, COD, Oil & Grease, and Phenols). Temperature and pH were measured immediately after sample collection.

pH was measured by a pH Ultrameter 6P , Myron L Company,  Carlsbad , CA. USA. Turbidity was measured by a 2100N Turbidimeter, HACH (NTU). For conductivity measurement ,712 Conductometer, Metrohm, was used. Alkalinity was determined by Titration Method. HACH DR/4000U spectrophotometer, CAMLAB limited, Cambridge, was used in all spectrophotometric determinations. BOD Incubator, Model 205, HACH, was used for BOD tests, whereas COD determination was performed using a COD reactor Model 45600, HACH. Heavy metals were determined by Atomic Absorption Spectrophotometer, VARIAN, SpectrAA 220FS Spectrometer FLAME AA with Varian SIPS-10 Sample Introduction Pump System , Varian SPS-5 Sample Preparation System , fully automated double beam system, and high intensity deuterium background correction as standard. All readings were made in duplicates and the average reading was taken.

**3.6.1 Physical parameters**

**3.6.1.1 Temperature**

Temperature readings were taken immediately at the sampling site using a mercury thermometer.

### 3.6.1.2 pH

pH determination was immediately carried out at the site using a portable pH meter.

### 3.6.1.3 Total solids (TS)

100 ml of well mixed sample were evaporated in a preweighed porcelain dish in a steam bath, then dried to a constant weight in an oven at $103^{\circ}$C.

**Calculation**

mg T.S/L $=$ $((A-B){\times}1000)/V$

Where:

A: weight of (dried solids + dish) in g.

B: weight of empty dish in g.

V: Volume of sample taken in ml.

### 3.6.1.4 Total dissolved solids (TDS)

200ml of well mixed sample were filtered into a 500 ml suction flask using a vacuum pump. 100 ml of the filtrate were transferred to a preweighed evaporating dish, and evaporated to dryness on a steam bath. Then the evaporated sample was dried in a drying oven at $180^{\circ}$C. mg TDS/L were calculated as in TS.

### 3.6.1.5 Total suspended solids (TSS)

The total suspended solids were determined by subtracting the total dissolved solids from the total solids calculated for each sample taken.

$$TSS = TS\text{-}TDS$$

### 3.6.1.6 Turbidity

Turbidity is an optical property that results from the scattering and absorption of light by colloidal or suspended particles present in the sample. The intensity of light scattered by the sample is compared with the intensity of light scattered by a standard solution.

The method applied is the Formazin Attenuation method using Formzin polymer as the primary standard reference suspension.

**Reagents**

(a) Dilution Water: deionized water was used as a low- turbidity water (<0.02NTU).

(b) Dilute Turbidity Suspensions: A commercial stock suspension of 4000 NTU formazin was diluted with deionized water to prepare 1000, 400, 200 and 20 NTU calibration standards.

**Procedure**

The nephelometer was calibrated using diluted standards of 4000, 1000, 400, 200 and 20 NTU, and deionized water was used as a blank. The sample was gently agitated and poured into sample cell after air bubbles disappeared. The reading was recorded directly without calculation in this digital nephelometer.

### 3.6.1.7 Conductivity

Conductivity generally measured with the aid of a conductivity meter. Conductance, when measured between the electrodes having a surface area of 1 $cm^2$ and placed at a distance of 1 cm, is called electrical conductivity and is the property of the wastewater sample, rather than the measuring system. A conductivity-meter was used to measure the conductivity of the waste water samples.

**Reagents**

(a) Conductivity Water: deionized water.

(b) Standard Potassium Chloride Solution (0.0100M): 745.6mg anhydrous KCI were dissolved in deionized water and diluted to 1000ml in a standard flask at $25^{\circ}C$.

**Procedure**

The probe was rinsed three times with 0.0100M KCl. This instrument is provided with automatic temperature compensation. The cell was rinsed with two portions of the sample and the conductivity was measured in μS/cm.

**3.6.2 Inorgaics**

**3.6.2.1 Alkalinity**

Total alkalinity of water or wastewater is the sum of all the titratable bases present in the sample, including carbonate, bicarbonate, hydroxide, borates, phosphates, silicates, or other bases if these are present. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate and hydroxide content, it is taken as an indication of the concentration of these constituents. Total alkalinity can be estimated by titrating the sample with a strong acid (HCl or $H_2SO_4$), first to pH 8.3 using phenolphthalein as an indicator and then further to pH between 4.2 and 5.4 with methyl orange or mixed indicator. In the first case, the value is called as phenolphthalein alkalinity (P) and in the second case, it is total alkalinity. Values of carbonates, bicarbonates and hydroxide ions can be computed from these two types of alkalinities.

The method used is the Titration Method. In this method soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response, therefore, additional time is allowed between titrant additions to let electrode come to equilibrium.

**Reagents**

(a) Sodium Carbonate Solution, 0.05N: 4.0 g of primary standard $Na_2CO_3$ were dried in an oven at $250^{\circ}C$ for 4 hours and cooled in a desiccator to room temperature. 2.5g of the dried salt were dissolved in deionized water and diluted to the mark in a 1L volumetric flask.

(b) Stock Solution of $H_2SO_4$, 0.1N: 500 ml deionized water were measured into a 1L volumetric flak. 2.8 ml conc $H_2SO_4$ were added slowly and diluted to the mark with deionized water.

(c) $H_2SO_4$ Standard Solution, 0.02N: 100 ml of 0.1N stock acid solution were measured into a 500 ml volumetric flask and diluted to the mark with deionized water.

$$1.0 \text{ ml } 0.02N \text{ acid solution} \equiv 1.0 \text{ mg } CaCO_3.$$

This acid solution was standardized using $0.05N \ Na_2CO_3$ solution.

(d) Phenolphthalein Indicator: phenolphthalein indicator solution was prepared by dissolving 0.5g phenolphthalein disodium salt in 1:1 ethanol and deionized water solution and diluting to the mark with deionized water in a 100ml volumetric flask.

(e) Methyl Orange Indicator: 0.05g powdered methyl orange were dissolved in deionized water and diluted to the mark in a 100ml volumetric flask.

(f) Mixed Indicator: 100mg bromocresol green sodium salt and 20mg methyl red sodium salt were dissolved in deionized water and diluted to the mark with deionized water in a 100ml volumetric flask.

**Procedure**

100 ml of unfiltered sample were transferred to a 250 ml beaker placed on a magnetic stirrer with a magnetic bar and pH meter electrodes inserted in the beaker. The solution was stirred, the initial pH and temperature were recorded and the solution was titrated to pH 8.3 with $0.02N \ H_2SO_4$ solution using phenolphthalein indicator, until the pink color disappeared. The volume of the titrant was recorded and this is the phenolphthalein end point (p). The titration was continued by adding 2 drops of mixed indicator unitl the color changed from greenish blue to red (pH 4.5). The volume of the titrant was recorded and this is the total alkalinity (T). A blank (100ml deionized water) was titrated by following the same procedure as described for the sample.

Alkalinity, mg/L as $CaCO_3 = \dfrac{(A-B) \times N \times 50000}{\text{ml sample}}$

Where:

    A = ml of 0.02 N $H_2SO_4$ used for the sample.

    B = ml of 0.02 N $H_2SO_4$ used for the blank.

    N = Normality of the acid.

The results obtained from the phenolphthalein (P) and total alkalinity (T) are related and stoichiometrically classify the three forms of alkalinity in wastewater, i.e. alkalinity due to hydroxide, carbonate and bicarbonate ions. The complete relationship scheme is give in Table (3.1).

**Table(3.1) :  Alkalinity relationships, (APHA 1989).**

| Result of titration | Hydroxide alkalinity as $CaCO_3$ | Carbonate alkalinity as $CaCO_3$ | Bicarbonate alkalinity as $CaCO_3$ |
|---|---|---|---|
| P=0 | 0 | 0 | T |
| P<1/2 T | 0 | 2P | T-2P |
| P= 1/2T | 0 | 2P | 0 |
| P>1/2T | 2P-T | 2(T-P) | 0 |
| P=T | T | 0 | 0 |

Where:

P = Phenolphthalein alkalinity.

T = Total alkalinity.

According to this scheme:

(a) Carbonate alkalinity is present when P is not zero but less than or equal to half T.

(b) Hydroxide alkalinity is present if P is more than T.

(c) Bicarbonate alkalinity is present if P equal to zero or less than half T.

**3.6.2.2 Hardness**

The Calmagite Colorimetric Method, used for hardness measurement in this study, supplements the conventional titrimetric method because the colorimetric method can measure very low levels of calcium and magnesium. Also some metals (e.g. $Cr^{3+}$, $Cu^{2+}$, $Fe^{2+}$, $Fe^{3+}$ , $Zn^{2+}$, and $Mn^{2+}$ ), that interfere in the titrimetric method may be inconsequential when diluting the sample to bring it within the range of this test. The indicator dye is calmagite, which forms a purplish – blue color in a strongly

alkaline solution and changes to red when contacting free calcium or magnesium. Calcium and magnesium determination are made by chelating calcium with EGTA to destroy any red color due to calcium and then chelating the calcium and magnesium with EDTA to destroy the red color due to both calcium and magnesium. By measuring the red color in the different states, calcium and magnesium concentrations are determined.

**Reagents**

(a) Calcium and Magnesium Indicator Solution.

(b) Alkali Solution for Calcium and Magnesium Test: (Sodium hydroxide).

(c) EDTA Solution (1.00M).

(d) EGTA Solution.

(e) Sodium Hydroxide Standard Solution (5.0 N).

**Calibration standards preparation**

(a) Calibration standards containing 0.5, 2.0, 2.5, 3.0, 3.5 and 4.0 mg/L Ca as $CaCO_3$ were prepared by transferring 1.00, 4.00, 5.00, 6.00, 7.00 and 8.00 ml of a 50 mg/L $CaCl_2$ standard solution as $CaCO_3$ into six different 100 ml volumetric flasks, diluted to the mark with deionized water and well mixed.

(b) Calibration Standards Containing 0.41, 1.65, 2.06, 2.47, 2.88 and 3.30 mg/L Mg as $CaCO_3$ were prepared as follows:

   (i) 10.00 ml of 1000 mg/L Magnesium standard solution as Mg were transferred to a 100 ml volumetric flask and diluted to the mark with deionized water to prepare a 100 mg/L standard (412 mg/L Mg as $CaCO_3$)

   (ii) 1.00, 4.00, 5.00, 6.00, 7.00 and 8.00 ml of the 100 mg/L magnesium standard were transferred into six different 1000 ml volumetric flasks and diluted to the mark with deionized water.

**Procedure**

Before analysis, the sample pH was adjusted to pH 6 with 5.0 N Sodium hydroxide standard solution. 100 ml of the sample were poured into a 100ml graduated mixing cylinder. 1.0 ml of calcium and magnesium indicator solution and 1.0 ml of

alkali solution for calcium and magnesium test were added using a 1.0 ml measuring dropper and the mixture was mixed. 25 ml of the solution were poured into each of three sample cells. One drop of 1.0 M EDTA solution was added to one cell (the blank) and one drop of EGTA solution was added to another cell (the prepared sample). After the instrument zero has been adjusted with the blank, the prepared sample was placed into the cell holder and the results in mg/L magnesium as calcium carbonate at wavelength ($\lambda$) 522nm were taken. This value is the amount of magnesium in the sample expressed as $CaCO_3$. Without removing the cell, the stored program for calcium harness was selected and the instrument was adjusted to zero. The third sample cell was placed in the cell holder and the result representing mg/L calcium in the sample was recorded.

### 3.6.2.3 Chloride

The method used for chloride determination is the Mercuric Thiocyanate Method. Chloride in the sample reacts with mercuric thiocyanate to form mercuric chloride and liberate thiocyanate ions, which in turn, react with the ferric ions to form an orange ferric thioeyanate complex. The amount of this complex is proportional to the chloride sample concentration. The chloride was determined at wavelength ($\lambda$) 455nm.

**Reagents**

Ferric Ion Solution: (perchloric acid, ferric perchlorate, water).

Mercuric Thiocyanate Solution: (mercuric thiocyanate, methyl alcohol).

**Calibration standard preparation**

To perform a chloride calibration in this method, a 100mg/L chloride stock solution was prepared by pipetting 50ml of 1000 mg/L chloride standard solution into a 500ml volumetric flask and diluting to the mark with deionized water. Calibration standards containing 3.00, 6.00, 9.00, 12.00, 15.00, 18.00 and 20.00 mg/L $Cl^-$ were prepared by pipetting 3.00, 6.00, 9.00, 12.00, 15.00, 18.00 and 20.00 ml of the 100.0 mg/L $Cl^-$ stock solution into seven different 100ml volumetric flasks and diluting to the mark with deionized water.

**Procedure**

Deionized water treated as the sample was used as a blank and calibration curve was generated using the standards prepared above.

The sample cell was filled with 25ml of the sample. 2.0 ml of mercuric thiocyanate and 1.0ml of ferric ion solution were added to the sample which was then placed into the cell holder after 2 minutes and the result in mg/L $Cl^-$ was recorded.

**3.6.2.4 Sulfate**

Sulfa Ver 4 Method was applied for the determination of sulfate in the sample. In this method, sulfate ions in the sample react with barium in the sulfa Ver 4 and form a precipitate of barium sulfate. The amount of turbidity formed is proportional to the sulfate concentration. The sulfa Ver 4 also contains a stabilizing agent to hold the precipitate in suspension. The measurement was done at wavelength ($\lambda$) 450nm.

**Reagents**

Sulfa Ver 4 Reagent: (barium chloride + stabilizing agent).

**Calibration standard preparation**

1, 2, 3, 4, 5, 6 and 7 ml of the 1000 mg/L sulfate standard solution were transferred to seven different 100 ml volumetric flasks and diluted to the mark with deionized water to prepare calibration standards containing 10, 20, 30, 40, 50, 60 and 70mg/L sulfate.

**Procedure**

Before running the sample the instrument zero has been adjusted against a blank (deionized water treated as the sample) and calibration was done using the prepared standards. The contents of one sulfa Ver 4 reagent powder pillow were added to 25 ml of the sample in the cell and mixed. A white turbidity was developed after 5 minutes. The sample was placed in the cell holder and the result in mg/L sulfate was recorded.

### 3.6.2.5 Sulfide

In Ethylene Blue Method, used for sulfide determination in this work, hydrogen sulfide and acid soluble sulfides react with N,N-dimethyl-p-phenylenediamine sulfate to form methylene blue. The intensity of the blue color is proportional to the sulfide concentration in the tested sample at the wave length ($\lambda$)665nm.

**Reagents**

Sulfide 1 Reagent : (N,N- dimethyl-p-phenylenediamine).

Sulfide 2 Reagent : (potassium dichromate).

**Procedure**

25 ml of the sample and 25 ml of deionized water (the blank), were measured into two separate cells. 1 ml of sulfide 1 reagent and 1 ml of sulfide 2 reagent were added to each cell. After a 5- minute reaction period, the instrument has been adjusted to zero by placing the blank in the cell holder. Then, the sample was placed in the cell holder and the result in µg/L sulfide was recorded.

### 3.6.2.6 Cyanide

The Pyridine- Pyrazalone Method, used for measuring the wastewater cyanide content in this work, gives an intense blue color with free cyanide which was neasured at ($\lambda$) 612 nm.

**Reagents**

(a) CyaniVer 3 Cyanide Reagent: (sodium phosphate, dibasic, halane, potassium phosphate, monobasic).

(b) CyaniVer 4 Cyanide Reagent: (ascorbic acid, pyridine-3-nitrophthalic acid, sodium sulfate).

(c) CyaniVer 5 Cyanide Reagent: (potassium phosphate, monobasic, sodium sulfate, 3- methyl-1- phenyl- 2- Pyrazoline-5-one).

**Calibration standard preparation**

A 100 mg cyanide stock solution was prepared by dissolving 0.1884g of pure sodium cyanide in deionized water and diluting to 1000ml. This solution was used in preparing working stardard solutions containing 0.05, 0.100 and 0.200mg/L

cyanide by pipetting 0.50,1.00 and 2.00ml into three different 1000 ml volumetric flasks, respectively and diluting with deionzed water to the mark.

**Procedure**

The spectrophotometer was zeroed using deionized water as blank and calibrated with the prepared standard solutions. Sample cell was filled with 10 ml of the sample using a graduated cylinder. The contents of one cyanic Ver 3 cyanide reagent powder pillow were added and the Stoppered sample cell was shaken for 30 seconds. After additional 30 seconds the contents of cyani Ver 4 cyanide reagent powder pillow were added and the cell was shaken for 10 seconds. Finally the contents of cyani Ver 5 cyanide reagent powder pillow were added and the cell was vigorously shaken, a pink color developed which then turned blue after a few minutes. After a 30- minute reaction period, the sample was placed into the cell holder and the result in mg/L cyanide was recorded.

### 3.6.2.7 Chromium (hexavalent)

Hexavalent chromium was determined by the 1,5- Diphenyl Carbohydrazide Method using a single dry powder formulation called chroma Ver 3 chromium reagent. This reagent contains an acidic buffer combined with 1,5- Diphenyl carbohydrazide, which reacts to give a purple color when hexavalent chromium is present and the intensity of the color is measured at 540nm.

**Reagents**

Chroma Ver 3 Chromium Reagent : (1,5-diphenylcarbohydrazide, magnesium sulfate, potassium pyrosulfate).

**Calibration standard preparation**

To perform a hexavalent chromium calibration using the 1,5- Diphenylcarbohydrazide method, a 5.0 mg/L chromium stock solution was prepared by pipetting 10.0 ml of a 50 mg/L hexavalent chromium standard solution into a 100 ml volumetric flask and diluting to the mark with deionized water and mixing thoroughly. Calibration standards containing  0.05, 0.30 and 0.60 mg/L $Cr^{6+}$ were prepared by pipetting 1.00, 6.00 and 12.00 ml of the 5.00 mg/L $Cr^{6+}$

stock solution into three different 100ml volumetric flasks ad diluting to the mark with deionized water and mixing thoroughly.

**Procedure**

A reagent blank was prepared using chromium – free deionized water in place of the sample to zero the instrument. For proof of accuracy the prepared standard solutions were used in place of the sample. The sample cell was filled with 10 ml of the sample and the contents of one chroma Ver. 3 reagent powder pillow were added to the sample cell and swirled. A purple color formed upon mixing indicating the presence of hexavalent chromium. After 8 minutes, the sample was placed into the cell holder and the result in mg/L hexavalent chromium was recorded.

### 3.6.3 Nutrients

### 3.6.3.1 Ammonia- nitrogen

The method used for the determination of ammonia- nitrogen in the sample is the Nessler Method in which the mineral stabilizer complexes hardness in the sample and the polyvinyl alcohol dispersing agent aids the color formation in the reaction of nessler reagent with ammonium ions. A yellow color formed is proportional to the ammonia concentration and measured at 425 nm.

**Reagents**

(a) Nessler Reagent : (mercuric iodide, sodium iodide, sodium hydroxide, demineralized water).

(b) Mineral Stabilizer : (potassium sodium tartarate, sodium citrate, demineralized water).

(c) Polyvinyl Alcohol Dispersing Agent.

(d) Sodium Hydroxide Standard Solution (5.0N).

**Calibration standard preparation**

For ammonia calibration using the Nessler Method, standard solutions containing 0.5, 1.0 and 2.0 mg/L ammonia- nitrogen were prepared by pipetting 0.5, 1.0 and 2.0 ml of the 100 mg/L ammonia- nitrogen standard solution into three different

100 ml volumetric flasks and diluting to the mark with deionized water and mixing thoroughly.

**Procedure**

The sample was neutralized with 5.0 N sodium hydroxide standard solution before analysis. Deionized water was used as a blank and the standard solutions prepared above were used to adjust the calibration curve. A 25-ml mixing graduated cylinder was filled to the mark with the sample. Three drops of the mineral stabilizer were added and the stoppered cylinder was inverted several times for mixing. Then three drops of polyvinyl acohol dispersing agent were added and the mixture was mixed. 1.0 ml of Nessler reagent was pipetted into the cylinder and the contents were mixed. A yellow color was developed and the solution was poured into the sample cell which was placed into the cell holder after a one minute reaction period. The result in mg/L ammonia expressed as nitrogen ($NH_3$-N) was recorded.

### 3.6.3.2 Nitrate-nitrogen

The method used to determine the nitrate in the wastewater samples is the Cadmium Reduction Method (Method 8039). In this method cadmium metal reduces nitrates in the sample to nitrite ion which reacts in acidic medium with sulfanilic acid to form an intermediate diazorium salt. The salt couples with gentisic acid to form an amber colored solution. The intensity of the color is measured at 500nm.

**Reagents**

Nitra Ver 5 Nitrate Reagent:   (cadmium, gentisic acid, magnesium sulfate, potassium phosphate, monobasic, sulfanilic acid).

**Calibration standard preparation**

For nitrate calibration using the Nitra Ver 5 Method, calibration standards containing 4, 14, and 30 mg/L nitrate- nitrogen were prepared by pipetting 2.00, 7.00 and 15.00 ml of a 1000 mg/L nitrate- nitrogen standard solution into three different 500 ml volumetric flasks and diluting to the mark with deionized water and mixing thoroughly.

**Procedure**

The sample cell was filled with 10 ml of the sample and the contents of one Nitra Ver 5 nitrate reagent powder pillow were added. The stoppered cell was shaken vigorously for one minute. After a 5- minute reaction period, the instrument was zeroed using a blank prepared by treating deionized water as for the sample and calibration was performed using the prepared calibration standards. Finally the sample was placed into the cell hoder and the result in mg/L nitrate- nitrogen was recorded.

### 3.6.3.3 Nitrite-nitrogen

Nitrite in the sample was determined by the Diazotization Method in which the nitrite reacts with sufanilic acid to form an intermediate diazonium salt in acid medium (pH 2-2.5). the salt couple with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite present. The color so produced obeys Beer's law and is measured at 507 nm.

**Reagents**

Nitri Ver 3 Nitrite Reagent: (1,2-cyclohexanediaminetetraaceticacid trisodium salt, chromotropic acid, disodium salt, potassium phosphate, monobasic, potassium pyrosulfate, sodium sulfanilate).

**Calibration standard preparation**

(a) A 100mg/L nitrite stock solution was prepared as follows:

(i) An adequate quantity of sodium nitrite was placed in a 50 ml beaker and kept for 24 h for drying in a desiccator containing conc. $H_2SO_4$.

(ii) 0.4928 g dried $NaNO_2$ were accurately weighed and dissolved in minimal volume of deionized water with stirring. The solution was transferred to a 1 L volumetric flask and diluted to the mark with deionized water.

1.0 ml stock nitrite solution $\equiv$ 100 $\mu$g $NO_2$–N

(b) 1.0 ml of the stock nitrite solution was measured in a 100 ml volumetric flask and diluted to the mark with deionized water to prepare a 1.0 mg/L standard nitrite solution.

1.0 ml standard nitrite solution $\equiv$ 1.00 µg NO$_2$ –N

(c) Calibration standards containing 0.10, 0.20 and 0.30 mg/L NO$_2$–N were prepared by measuring 10.0, 20.0 and 30.0 ml of the standard nitrite solution into three different volumetric flasks and diluting to the mark with deionized water.

**Procedure**

A sample cell was filled with 10 ml of the sample. The contents of one Nitri Ver 3 Nitrite reagent powder pillow were added and the stoppered cell was shaken to dissolve the reagent. After a 20 minute reaction period the instrument was adjusted to zero with deionized water (the blank). The calibration was performed using the prepared calibration standards. The result in mg/L nitrite nitrogen was recorded after placing the sample into the cell holder.

**3.6.3.4 Phosphorus – ortho (reactive)**

Phosphorus in water and wastewater generally occurs in the form of ortho-phosphates, polyphosphates (meta-, pyro- or other polyphosphates), and organic phosphates, **(Tomar 1999)**. One of the most reactive forms is ortho- phosphate which includes phosphate (PO$_4^{3-}$), hydrogen phosphate (HPO$_4^{2-}$) dihydrogen phosphate (H$_2$PO$_4^-$) and phosphoric acid (H$_3$PO$_4$). Polyphosphates include the molecules with two or more P atoms forming complex molecules. Organic phosphates are the products of various biological degradation processes. Ortho-phosphate can be determined directly with ammonium molybdate. All other forms of phosphorus must be converted into ortho-phosphorus before estimation. The digestion of the sample under different conditions can do this separation. The complete analytical scheme to separate various forms of phosphorus is presented in Figure 3.4
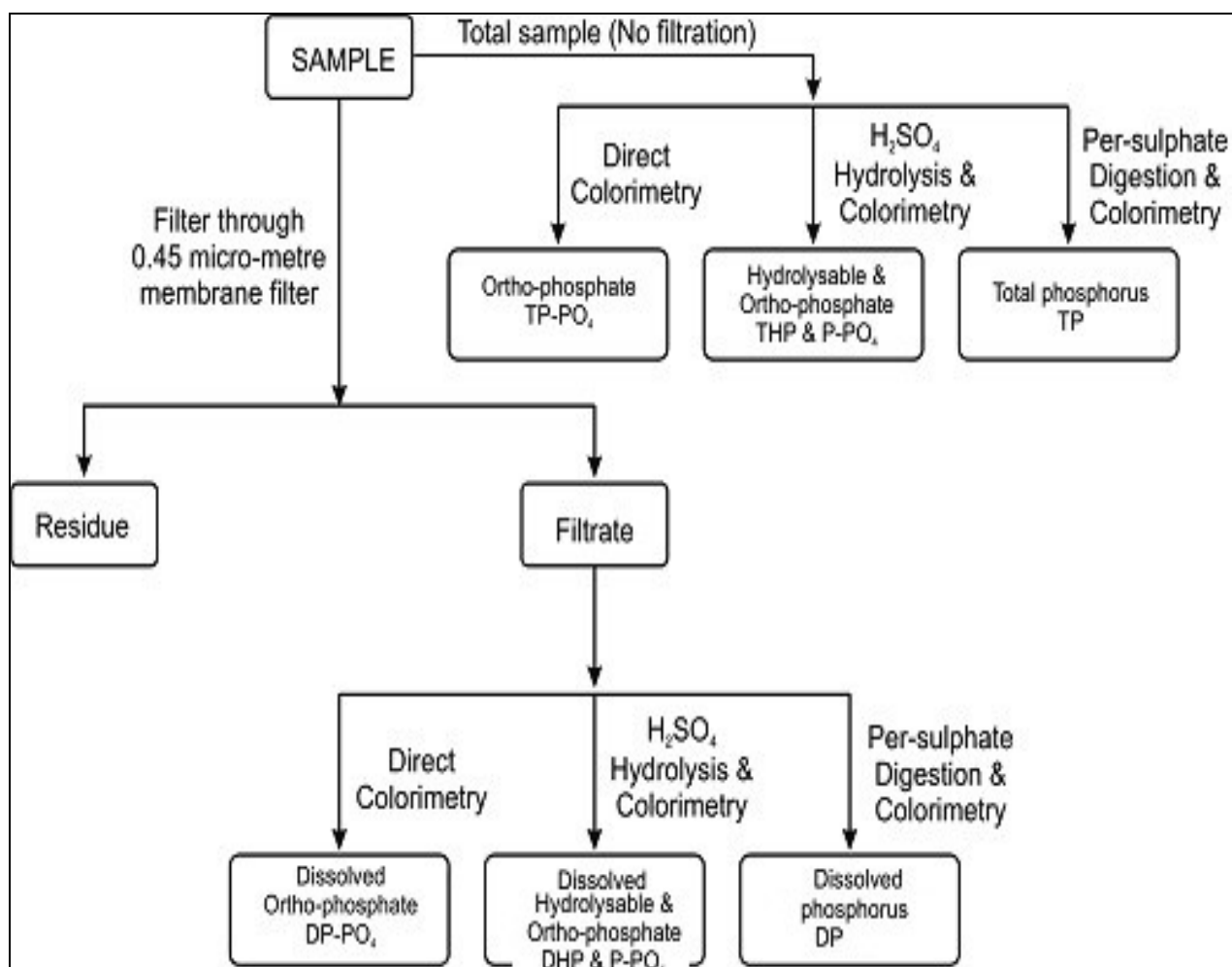
**Figure 3.4:** Analytical scheme for differentiation of various phosphorus forms in water and wastewater. Source: US EPA (1983)

Reactive phosphorus in the present study was determined by the Ascorbic Acid Method. Phosphorus present in the form of ortho- phosphate, which is known as reactive phosphorus, complexes with molybdate under acidic conditions producing a phosphomolybdate complex. Ascorbic acid then reduces this complex producing an intense blue – colored molybdenum complex proportional to the ortho-phosphate concentration.

**Reagents**

(a) Cleaning Solution, HCl 50% (v/v) : 100ml conc. HCl added to 100 ml deionized water.

(b) Sulfuric Acid : concentrated.

(c) Complexing Reagent :

(i) 0.13g of antimony potassium tartarate $[k(SbO)C_4H_4O_6\, 0.5H_2O)]$ were weighed and transferred to a 1 L volumetric flask and dissolved in 500 ml deionized water.

(ii) 5.6g ammonium molybdate were added to the above solution and swirled until it dissolved completely.

(iii) 70ml conc. $H_2SO_4$ were slowly added with continuous stirring. The solution was cooled and diluted to the mark with dionized water.

(d) Combined reagent :

0.5 g ascorbic acid were weighed and transferred to a 100 ml volumetric flask and then, dissolved in 100 ml complexing agent prepared in step (c).

(e) Phosphorus Stock Solution, $KH_2PO_4$ :

(i) An adequate quantity of anhydrous Potassium dihydrogen phosphate was dried for 1 h in an oven set at 105°C and then, cooled to room temperature in a desiccating cabinet.

(ii) 0.4394g dry and cool $KH_2PO_4$ were accurately weighed , transferred to a 1 L volumetric fask , dissolved in deionized water, and diluted to the mark.

1.0 ml stock solution $\equiv$ 0.1 mg $PO_4^{3-}$–P

(f) Phosphorus Standard Solution :10 ml phosphorus stock solution were measured in a 100 ml volumetric flask and the volume brought to the mark with deionized water.

1ml standard solution $\equiv$ 0.01 mg $PO_4^{3-}$–P

**Calibration standard preparation**

Calibration standards containing 1.0, 3.0, 5.0 and 7.0 mg/L phosphate were prepared as follows:

5, 15, 25 and 35 ml standard phosphorus solution were measured into four different 50 ml volumetric flasks.The solution in each flak was diluted to the mark with deionized water.

**Procedure**

All the glassware rinsed with the cleaning solution and washed thoroughly with deionized water. 50 ml sample (without filtration) were measured into a 100 ml Erlenmeyer flask and 10 ml of combined reagent were added and mixed thoroughly by swirling the flask several times. After a 20 minute reaction period the instrument was adjusted to zero with deionized water and the calibration was performed using the prepared calibration standards. The sample was placed into the cell holder and result in mg/L $PO_4^{3-}$ - P was recorded.

### 3.6.3.5 Phosphorus – total recoverable

The Digestion Method was applied for the determination of total phosphorus in the samples. The sample is digested with acid–persulfate mixture which converts all the forms of phosphorus ,including organic and inorganic phosphates, to ortho-phosphates. After digestion total phosphorus is measured quantitatively with the Ascorbic Acid Procedure followed for the ortho-phosphate determination.

**Reagents**

(a) Cleaning Solution HCl 50% (v/v): Prepared as in the estimation of ortho-phosphate.

(b) Sulfuric Acid (9.0N): 500 ml deionized water were measured in a 1L volumetric flask. 250 ml conc. $H_2SO_4$ were added slowly with cooling and diluted to the mark with deionized water. Finally the solution was mixed and cooled.

(c) Sodium Hydroxide (2.0N): 40g NaOH were weighed and transferred to a 500 ml volumetric flask. 300 ml boiled and cooled deionized water was added to dissolve the salt. Then the cooled solution was diluted to the mark with remaining deionized water.

(d) Phenolphthalein Indicator: commercially ready –made solution.

(e) Ammonium Persulfate: powder chemical.

**Procedure**

**Sample digestion**

All glassware were rinsed with cleaning solution and washed thoroughly with deionized water. 25 ml sample (without filtration) were measured into a 125 ml Erlenmeyer flask and cleaned glass beads were placed into the flask. 0.5 g ammonium persulfate powder were added with swirling to mix the contents. 1.0 ml of 9.0 N $H_2SO_4$ solution was added, the flask was covered with aluminum foil and boiled gently for 30 minutes in a hot plate with volume maintained near 20 ml by adding small volumes of deionized water. After 30 minutes digestion 5 drops of phenolphthalein. After 30 minute digestion, 5 drops of phenolphthalein indicator were added to the cooled solution followed by dropwise addition of 2.0N NaOH solution until a pink color appeared. $H_2SO_4$ solution was added slowly to discharge the pink color. The sample was poured into a 25 ml graduated cylinder with the volume adjusted to 25 ml. This solution was used to estimate the total phosphorus content in the sample following the procedure used for ortho-phosphate estimation. The result in mg/L ($PO_4^{3-}$ -P) total was recorded.

### 3.6.4 Organics

### 3.6.4.1 Phenols

The 4- Aminoantipyrine Method was applied for the determination of phenols in the wastewater samples. It is capable to measure all ortho- and meta- substituted phenols. The sample is distilled to remove interfering substances such as oxidizing compounds, sulfer compounds , oils, and tars. The phenols present in the distilled sample react with 4- Aminoantipyrine in the presence of potassium ferricyanide to form a colored antipyrine dye that is then extracted from the aqueous phase with chloroform and the color is measured at 460nm. The sensitivity of the method varies with the type of phenolic compound.  Since wastewater may contain various types of phenolic compounds the analytical results are expressed as mg/L of phenol ($C_6H_5OH$).

**Reagents**

(a) Methyl Orange Indicator : 0.5g/L solution.

(b) Phosphoric Acid Solution : 10% (v/v).

(c) Chloroform ACS.

(d) Hardness 1 Buffer Solution, pH 10.1.

(e) Phenol 2 Reagent : (potassium sulfate, potassium ferricyanide).

(f) Phenol Reagent: (Sodium sulfate, 4-Aminoantityrine hydrogen phosphate).

**Calibration standard preparation**

(i) Phenol Stock Solution : 1.00g phenol ACS was dissolved in freshly boiled and cooled deionized water and diluted to 1000ml to prepare a 1000mg/L phenol stock solution.

(ii) Phenol Working Solution: 10.0 ml of the 1000 mg/L stock solution were transferred into a 1000ml standard flask and diluted to the mark with deionized water to prepare a 10.0 mg/L phenol working solution.

(iii) Phenol Standard Solution : standards containing 0.02, 0.08, 0.16 and 0.20 mg/L phenol were prepared by transferring 1.0, 4.0, 8.0 and 10.0 ml of the 10 mg/L working solution into four different 500ml volumetric flaks and diluting to the mark with deionized water.

**Distillation of the sample**

The distillation apparatus was seted up using a 500ml erlenmeyer flask to collect the distillate with a stirring bar placed in it. 300 ml of the sample were measured into the distillation flask with a clean graduated cylinder and 1.0 ml of methyl orange indicator was added. The stirrer was turned on for thorough mixing and 10% phosphoric acid was added drop-wise until the indicator color changed from yellow to orange. The distillation flask was closed and the water was turned on and adjusted so that a constant flow was maintained through the condenser. The heater was turned on and seted to control position 10. 275 ml of the distillate were collected in the erlenmeyer flask, then the heater was turned off. 25 ml warm deionized water were added to the distillation flask and The heater turned on

again collecting another 25ml of the distillate. The heater was turned off and 300 ml of the distillate were measured in a flask. This distillate was used for the measurement of phenol content in the sample.

**Procedure**

300 ml deionized water and 300 ml distilled sample were measured respectively into different 500 ml separatory funnels using a 500 ml graduated cylinder. 5 ml of hardness 1 buffer were added to each separatory funnel and the stoppered funnels were shaken. The content of one phenol reagent powder pillow was added to each separatory funnel and shaking process was repeated.  The contents of one phenol 2 reagent powder pillow were added to each separatory funnel, followed by shaking.30 ml chloroform were added and each of the stoppered funnels was inverted and temporarily vented. Then each funnel was vigorously shaken for 30 seconds. Both funnels were allowed to stand without stoppers until the chloroform settled to the bottom. A large pea-sized cotton plug was inserted into the delivery tube of each funnel and subsequently the chloroform layers were drained into separate sample cells; 25ml for the blank and 25ml for the sample ( filtering the chloroform layer through the cotton was found to remove the suspended water or particles). The blank was used in adjusting to zero and the phenol standard solutions prepared above were used for calibration. Then the sample was placed into the cell holder and the result in mg/L phenols was recorded.

**3.6.4.2 Oil and grease (Oil & G)**

The method used is the Partition Gravimetric Method. The procedure involves the extraction of oil and grease with an organic solvent 1,1,1- trichloroethane. The two immiscible solvents (organic solvent and water) make separate layers. The solvent containing the oil and grease fraction of the wastewater is separated from the aqueous layer. It is dried and evaporated to determine the extractable residue by the gravimetric method.

**Reagents**

(a) Extracting solvent: 1, 1, 1-trichloroethane, $CCl_3$-$CH_3$.

(b) $Na_2SO_4$ : anhydrous salt.

**Procedure**

All glassware were rinsed with 1, 1, 1-trichloroethane solvent to remove any traces of oil/grease. The boiling flask and clean glass beads were dried in an oven adjusted to 103°C for 1 hour, then cooled to room temperature in a desiccating cabinet and the flask with beads were weighed to a constant weight. 1 L of the sample was transferred to a separatory funnel of 2 L capacity then, the sampling bottle was rinsed with 20 ml solvent and the washings were transferred into the separatory funnel. This procedure was repeated three times and the separatory funnel was vigorously shaken for 2 minutes. The solution was allowed to stand for 10 minutes for clear separation of the extracting solvent and the water layers. The extraction procedure was repeated and the solution was allowed again to stand for 10 minutes. The extracting solvent layer was passed into the pre-weighed boiling flask through a funnel with a whatman paper cone. The bottle was rinsed three times more with 60 ml of the solvent and each extraction layer was transferred to the boiling flask containing the first solvent layer. Then the solvent was evaporated to dryness in a distillation unit with the heating mantle adjusted at 70°C. The exterior of the cool boiling flask was carefully wiped with an absorbent clean cloth and a small amount of acetone to remove any traces of water and fingerprints. Then the boiling flask was placed in a desiccator for 1 hour and weighed immediately. The process of desiccating and weighing was repeated until a constant weight was obtained. A blank was run using 1 L deionized water following the same procedure as described for the sample.

Calculation:

$$\text{Oil/Grease, mg/L} = \frac{(A - B) - C}{\text{Volume of sample, ml}} \times 1000$$

Where:

A= total weight of (flask + beads + residue)

B= weight of (flask + beads)

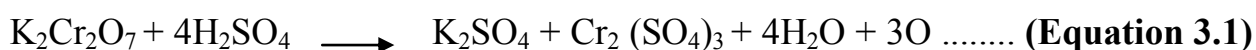C = average blank determination (residue obtained from deionzed water)

In the above procedure, 1L sample was taken for the determination of oil and grease content, hence the calculation was further modified as follows:

Oil/Grease, mg/L = (A–B) – C

### 3.6.4.3 Chemical oxygen demand (COD)

The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter susceptible to oxidation by strong oxidizing chemicals. It is an important representation of pollution level of industrial wastewater and has an advantage in that it requires a short digestion period as compared with biochemical oxygen demand. Hence, a rapid and frequent monitoring of treatment plant efficiency can be maintained wit COD measurement.

The wastewater samples in this work were tested for their COD content by The Reactor Digestion Method. In this closed reflux, colorimetric method the organic matter is converted to $CO_2$ and $H_2O$ by heating with potassium dichromate in an acidic medium. The nascent oxygen produced in the reaction **Equation 3.1** oxidizes the organic matter as shown in **Equation 3.2 :**

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O ........ \textbf{(Equation 3.1)}$$

$$Organic\ Matter + O \longrightarrow CO_2 + H_2O .......................................... \textbf{(Equation 3.2)}$$

The dichromate is reduced to $Cr^{3+}$ state, which imparts green color to the reacting solution. The overall reaction is presented in **Equation 3.3 :**

$$Organic\ Matter + Cr_2O_7^{2-} + H^+ \longrightarrow CO_2 + H_2O + Cr^{3+} ............. \textbf{(Equation 3.3)}$$

Both of these chromium species (i.e. the hexavalent (VI) state and the trivalent (III) state) are colored and absorb in the visible region of the spectrum. The dichromate ion absorbs strongly in the 40 nm region, where the chromic ion absorption is much less. The chromic ion absorbs strongly in the 600 nm region, where the dichromate has nearly zero absorption. For COD values between 0 and 150mg/L the amount of $Cr^{6+}$ at 420 nm is determined. COD values between 150 and 1500mg/L can be determined by measuring the amount of $Cr^{3+}$ produced at 620nm. Straight-chain aliphatic compounds, aromatic compounds and pyridine resist oxidation and volatile organic compounds will react in proportion to their contact with the oxidant. However, straight-chain aliphatic compounds are oxidized more effectively in the presence of silver sulfate catalyst which is used in this procedure and the volatile organic compounds are more completely oxidized in the closed system because of longer contact with the oxidant. Chloride ion interferes by restricting the oxidizing action of the dichromate ion and reacting with silver ion to precipitate silver chloride and thus inhibits the catalytic activity of silver. These difficulties can be overcomed largely by complexing the chloride ion with mercuric sulfate prior to refluxing in this method.

**Reagents**

COD Digestion Reagent, high range (0-1500mg/L COD) :

(Sulfuric acid 86%, Mercury sulfate, chromium trioxide).

**Calibration standard preparation**

(a) COD Stock Solution: 0.85g of dried (120°C, overnight) potassium hydrogen phthalate were dissolved in deionized water and diluted to 100ml to prepare a 10000mg/L COD stock solution.

(b) Calibration Standard Solution: calibration standards containing 200, 600, 1000, 1400 and 1600 mg/L COD were prepared by transferring 2.0, 6.0, 10.0, 14.0 and 16.0 ml of the 10000mg/L COD stock solution into five different 100ml volumetric flasks and diluting to the mark with deionized water.

**Procedure**

**(a) Digestion**

100ml of the sample were homogenized for 30 seconds in a blender. The COD reactor was turned on and preheated to 150°C with the plastic shield placed in front of the reactor. The cap of a high range COD digestion reagent vial was removed. 2.00 ml of the sample were pipetted into the vial holded at 45°C angle. The vial cap was replaced tightly and the vial was rinsed with deionized water and wiped clean with a paper towel. Then the vial was inverted several times to mix the contents and placed in the preheated COD reactor. A blank was prepared by repeating the above steps substituting 2.00 ml deionized water for the sample and placing the blank in the reactor. Then the vials were heated for 2 hours. The reactor was turned off and waited for 20 minutes for the vials to cool to 120°C. Each vial was inverted several times while still warm, then, the vials were left in a rack to cool to room temperature.

**(b) Measurement**

The test N tube adapter was inserted into the sample cell module. The outside cleaned blank was placed into the adapter and the instrument was adjusted to zero. The instrument calibration was performed using the calibration standard solutions prepared above. The outside cleaned sample vial was placed into the adapter and result in mg/L COD was recorded.

### 3.6.4.4 Biochemical oxygen demand (BOD)

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of water, effluents and polluted waters. Biochemical oxygen demand is the representation of the amount of oxygen required for microbial decomposition, i.e., complete aerobic decay and mineralization of biodegradable organic matter present in water or wastewater. The aerobic decomposition involves the breakdown of complex organic molecules into their simpler constituents that

can serve as food for the growth and activity of microbes and liberate energy in the presence of dissolved oxygen (DO).

The aerobic decomposition of organics takes place in two stages:

(a) Carbonaceous oxidation: This is the first stage in which mainly the carbonaceous (carbon fraction) matter is oxidized. Generally it reaches to maximum stabilization in five days **(Equation 3.4) :**

$$DO + Organic\ Matter \xrightarrow{\text{bacteria and protozoa}} CO_2 + H_2 + microbial\ cells \text{ ......}\textbf{(Equation 3.4)}$$
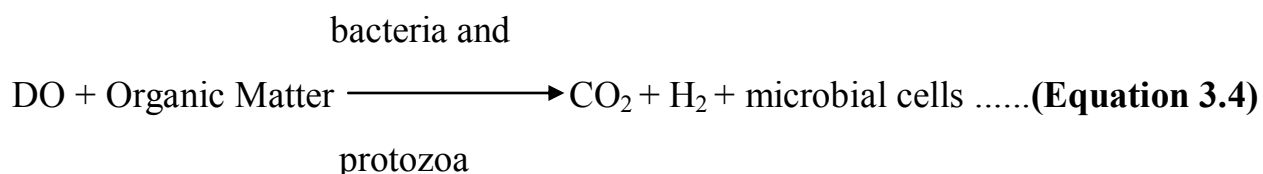
(b) Nitrogenous oxidation: In this second stage, nitrogenous (nitrogen – containing) substances such as ammonia are attacked by bacteria and develop a demand of oxygen as shown in **Equation 3.5** below:

$$DO + NH_3 - N \xrightarrow{\text{nitrifying bacteria}} NO_3 - N + microbial\ cells \text{ ............}\textbf{( Equation 3.5)}$$
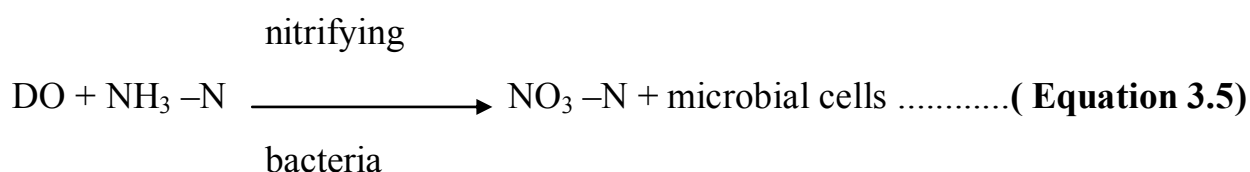
For the purpose of wastewater treatment, the first stage oxygen demand is considered BOD because the maximum carbonaceous components of organic matter are stabilized. The stabilization is maximum (96%) in five days **(Tomar, 1999)**, hence the term BOD is generally represented as BODs which means the oxidation of organic wastewater in five- days at 20°C. The extent of oxidation of nitrogenous compounds during the five - days incubation depends on the presence of nitrifying bacteria. Usually during this period the nitrogenous oxidation does not begin because nitrifying bacteria are not available in sufficient number in primary effluent. However, for samples of secondary effluent and for samples of polluted waters the interference from nitrogenous demand can be prevented by an inhibitory chemical.

The Dissolved Oxygen Dilution Method was used to determine the BOD levels in the present work. The method consists of filling with diluted and seeded sample, to overflowing, an airtight bottle of specified size and incubating it at the specified temperature for 5 days. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement.

**Regents**

(a) Phosphate buffer solution: 8.5g $KH_2PO_4$, 21.75g $K_2HPO_4$, 33.4g $Na_2HPO_4.7H_2O$, and 1.7g $NH_4Cl$ were dissolved in 500 ml DDW and diluted to 1 L ( pH 7.2).

(b) Magnesium sulfate solution: 22.5g $MgSO_4.7H_2O$ were dissolved in DDW  and diluted to 1L.

(c) Calcium chloride solution: 27.5g $CaCl_2$ were dissolved in DDW and diluted to 1L.

(d) Ferric chloride solution: 0.25g $FeCl_3.6H_2O$ were dissolved in DDW and diluted to 1L.

(e)Acid and alkali solutions, 1N, for neutralization of caustic or acidic waste samples.

  (i) Acid :  28 mL conc sulfuric acid were added Slowly, while stirring, to DDW and diluted to 1 L.

  (ii) Alkali : 40 g sodium hydroxide were dissolved in DDW and diluted to 1L.

(f) Nitrification inhibitor, 2-chloro-6-(trichloromethyl) pyridine: chemical powder.

(g) Glucose- glutamic acid solution : glucose and glucamic acid were dried at 103°C for 1h. 150mg glucose and 150mg glutamic acid were added to DDW and diluted to 1L.

(h) Ammonium chloride solution: 1.15 g $NH_4Cl$ were dissolved in about 500mL DDW, PH adjusted to 7.2 with NaOH solution , and diluted to 1L. Solution contains 0.3 mg N/mL.

(i) Seed :   From domestic raw sewage.

(j) Dilution water : 1 mL each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solution were transferred into a glass flask and completed to 1L with distilled water. The dilution water was aerated by shaking to obtain DO concentration > 7.5mg/L and the temperature was brought to 20°C. The dilution water was tested by filling a 300mL BOD bottle, stoppered tightly without entrapment of air bubbles, and incubated for five days at 20°C. The DO depletion was less than 0.2 mg/L.

**Testing procedure**

(a) Seeded dilution water : 2mL of seed per 1mL of diluted sample.Used for dilution of samples.

(b) Sample preparation and pretreatment: Sample temperature was   adjusted to 20 °C, then pH to 7.0 to 7.2 using sulfuric acid solution (1N).

(c) Sample dilution : 30 mL sample were added to individual BOD bottles Using a wide - tip volumetric   pipettes . Each BOD bottle was filled approximately two-thirds full with dilution water. Appropriate amounts of seeds suspension and nitrification inhibitor were added to the individual BOD bottles which are then completely filled with dilution water, sealed, and stoppered carefully without entrapment of air bubbles.

(d) BOD measurement :  For each sample, one 300 mL glass stoppered BOD  bottle filled with diluted sample and the other with dilution water only as a blank ,were prepared. The initial DO was measured immediately in the two bottles using a DO probe with replacement of displaced contents with sufficient diluted sample or dilution water to fill the bottles,which were stoppered tightly, and water sealed. The bottles were incubated for 5 days  at 20°C. Each sample was done in duplicate.

After 5 days of incubation, DO was determined in all sample dilutions, and in all blanks using the membrane electrode method. BOD was calculated as follows :

$$BOD_5, mg/L = \frac{(D_1 - D_2) - (S)Vs}{P}$$

Where:

$D_1$ = DO of diluted sample immediately after preparation, mg/L.

$D_2$ = DO of diluted sample after 5 d incubation at 20°C, mg/L.

S = oxygen uptake of seed, _ DO/mL seed suspension added per bottle, (S = 0 if samples are not seeded).

Vs = volume of seed in the respective test bottle, mL.

P = decimal volumetric fraction of sample used; 1/P = dilution factor.

### 3.6.5 Heavy metals

The wastewater samples were digested with conc. nitric acid and analyzed for the metals Fe, Ni, Cu, Cr, Cd, Ba, Pb, Zn, Ag, and Se using Flame Atomic Absorption Spectrophotometer.

### Nitric acid digestion method

100ml of acid preserved sample were transferred to a 125 ml beaker. 5 ml of conc. nitric acid and some boiling chips were added and the contents were evaporated on the hot plate to about 10ml. The beaker was cooled and another 5 ml of conc. nitric acid were added. The beaker was covered with a watch glass and returned to the hot plate. The temperature was adjusted in such a way that a gentle refluxing occured without boiling the solution. The completion of digestion was indicated by the appearance of light- colored, clear solution. The beaker walls and watch glass were washed with minimum deionized water and the solution was filtered. The filtrate was transferred to a 100ml volumetric flask with 5 ml portion of deionized water used for rinsing. The solution was cooled and diluted to the mark with deionized water. A reagent blank was digested using the same procedure with dionized water instead of the sample.

**Preparation of standard solution**

A multi element standard solution (0.1mg ml$^{-1}$) was prepared by approprite dilution of AAS standard metal solution (1000μg ml $^{-1}$)purchased from Merck (Darmstat, Germany). Working standard solutions of Fe, Ni, Cu , Cr, Cd, Ba, Pb , Zn , Ag and Se were prepared by a appropriate dilution of multielement standards with deionzed water.

**Determination of heavy metals**

The AAS was adjusted to zero against the blank and calibrated for each element by aspirating the working standard solutions. The concentration of each element was read in ppm and each analyis carried out in duplicates.

**3.7 Sediment Analysis**

The samples for atomic absorption spectrometry (AAS) should be in liquid form. There for the sediment samples should be brought into solution by wet digestion using strong acids at high temperature. The samples were analyzed for the metals Fe, Ni, Cu, Cr, Cd, Ba, Pb, Zn, and Ag using Flame Atomic Absorption Spectrophotometer.

**3.7.1 Sample preparation for AAS**

Prior to digestion the pretreated sediment samples were oven– dried at 105°C at the time of analysis and completely digested with a mixture of concentrated acids, $HNO_3$-HF- $HClO_4$, following the procedure applied by **Nakashima *et al*., (1988)**, with modifications in the system and consequently in digestion duration.

**" Total" acid digestion procedure**

For total metals concentration, the < 45 μm sediment fraction was subjected to an acid digestion procedure. A mass of 0.5g of each dry sediment sample was weighed into 100mL teflon beaker. 4 ml conc. $HNO_3$ and 2 ml conc. HF were added and the beakers were loosely capped and left to stand overnight at room temperature for initial (cold) digestion (i.e. digestion of organic matter). Cold predigestion was found to be necessary to a chieve complete dissolution of all sample contituents except silicates. subsequently 10 ml conc. $HClO_4$ were added to

the mixture. The teflon beakers were tightly stoppered to reflux the vapours of the acids and heated on a sand bath at 350°C for 6 hours, until complete digestion was achieved which was indicated by the non–turbid yellow–white solution appearance. Then the solution was evaporated to near dryness, the corners and walls of the beakers were washed with deionised water and the combined solution- washings were filtered by whatman filter paper into a 50 ml volumetric flask. The filter papar was washed with small volumes of 10% (v/v) $HNO_3$ and deionised water and the volume was completed to the mark with deionized water. The prepared solutions were stored in 100-ml polyethylene bottles at room temperature for further analysis.

**Preparation of standard solution**

As described in **section 3.6.5**

**3.7.2 Quality Control**

Validation of the total acid digestion method presented in this study was performed by standard reference material from the International Atomic Energy Agency (IAEA-Soil- 7), analytical quality control services; Vienna, Austria. It was digested using the nitric, hydrofluoric, perchloric acids digestion method. This was done as a reference for quality control and assurance of the method.

**3.7.3 Quality Assurance**

In all cases, all chemicals and reagents used were of analytical reagent grade and deionized water was used through out the experiments. All glass ware and plastic-ware previously cleaned and soaked in 10% (v/v) $HNO_3$ and rinsed with deionized water, blanks were run where necssary and each analysis carried out in duplicate.

**3.7.4 Instrumentation**

A VARIAN Atomic Absorption Spectrometer model SpectrAA 220FS was used for the determination of all the elements after successive dissolution, decomposition and made up to the 50ml mark in a volumetric flask.

# Chapter Four
# Results and Discussion

Very limited studies have been completed on quality of liquid effluents of Khartoum Petroleum Refinery, including Faris and Abdel-Magid **(2003)**, and Khogali **(2005)** as mentioned previously in section 1.5. Therefore, there is a need for a new full survey of liquid effluent quality and environmental assessment in the refinery in this research project.

This section presents the results of physical properties (Temperature, pH, TS,TDS, TSS, Conductivity, and Turbidity), inorganics (alkalinity, hardness, chloride, sulfate, cyanide, sulfide, and hexavalent chromium), nutrients (ammonia-nitrogen, nitrate- nitrogen, nitrite- nitrogen, and phosphorus), organics (BOD, COD, oil and grease, and phenols) and heavy metals (Cr, Cd, Ni, Fe, Pb, Zn, Ba, Ag, Se and Cu) as determined in samples collected from effluents of Khartoum Refinery monitoring pond and oxidation ponds (pond (A), pond (B), and pond (C)). Also results of heavy metals determined in oxidation ponds sediments are presented in this section. The data in the tables and figures comprehensively tell where and what concentration is highest or lowest for each of the parameters in relation to what has been obtained in this study and what the effluent limitation guidelines (if specified) should be. The obtained results also compared with the Food and Agriculture Organization of the United Nations (FAO) guidelines for irrigation water and the World Health Organization (WHO) guidelines for drinking water to assess Khartoum Refinery effluent in terms of irrigation quality and suitability for discharge into freshwater bodies respectively. The effluent limitation guidelines were taken from the Ministry of Energy and Mining, Sudan **(MEM, 2005)**, Environment Department of the World Bank **(WB, 1998)**, International Finance Corporation, World Bank Group **(IFC, 2007)**, Ontario Ministry of the Environment, Canada **(OME, 1992)**, Ministry of Environment and Forests, India

**(MEF, 2008)**, Federal Environmental Protection Agency, Nigeria **(FEPA, 1991)**, Food and Agriculture Organization of the United Nations **(FAO, 1985)**, and World Health Organization **(WHO, 2011)**.

## 4.1 Monitoring Pond (MP) Effluent Quality

The quantity of wastewaters generated from a petroleum refinery and their characteristics depend on the process configuration. As a general guide, ap proximately 3.5–5 cubic meters ($m^3$) of wastewater per ton of crude are generated when cooling water is recycled. Refineries generate polluted wastewaters, containing biochemical oxygen demand (BOD) and chemical oxygen demand (COD) levels of approximately 150–250 (mg/l) and 300–600 mg/l, respectively; phenol levels of 20–200 mg/l; oil levels of 100–300 mg/l in desalter water and up to 5,000 mg/l in tank bottoms; benzene levels of 1–100 mg/l; benzo(a)pyrene levels of less than 1 to 100 mg/l; heavy metals levels of 0.1–100 mg/l for chrome and 0.2–10 mg/l for lead; and other pollutants, (**WB, 1998**). Treatment processes in Khartoum Refinery are intended to improve the quality of the effluents which are then discharged to the MP through the sedimentation tank and filters. MP is considered the most important monitoring check point , therefor, the analyses results of the samples taken check the whole treatment processes. This is because of that effluents are discharged right way to the environment through the oxidation ponds without further treatment. MP effluent is a combination of treated process wastewater and non-process wastewater.

The physical, inorganics, nutrients, and organics qualities of MP effluents generated in Khartoum refinery were investigated, and the level of contaminants estimated. The concentrations of the most significant pollutants in the pond effluents are presented in Tables 4.2− 4.5.

### 4.1.1 Physical parameters

Table 4.2 shows the results of the physical quality analysis of wastewater samples collected from MP. The data generaly indicates high levels of all the measured parameters with variations in compliance with recommended limits.

### 4.1.1.1 Temperature

This is a measurement of the intensity (not amount) of heat stored in a volume of water. Water used in petroleum refinery as a process fluid where water, in the form of steam, is required in many refining process units to come into contact with hydrocarbons to facilitate processing and in the form of condensate where wash water is used primarily for corrosion control. Also water is used as a heating fluid (steam for heating purposes) and as a cooling fluid **(CFA, 2013)**. Water originates from these processes usually is characterized by its high temperature.

Temperature measurements of MP effluent in three consecutive days revealed fluctuation and large temperature increase when compared with the ambient temperature. The increase was 16°C (38−22) in the first day, 7.5°C (40−32.5) in the second day, and 12.5°C (39−26.5) in the third day (shown only the average in Table 4.2). The average temperature increase was 12°C which is largely exceeding the standard limits of the World Bank **(WB, 1998)** and International Finance Corporation **(IFC, 2007)** of ≤ 3, Ministry of Environment and Forests, India **(MEF, 2008)** of ≤ 5, and Federal Environment Protection Agency, Nigeria which sets a maximum effluent temperature of 30°C **(FEPA, 1991)**. Also according to the World Health Organization standard for effluent temperature to be discharged into water bodies or environment, the temperatures of the effluent samples were above the permissible limit of 30°C **(WHO, 2011)**.

This heated effluent when returned to the natural environment at a higher temperature , it could affect ecosystem composition and impact organisms by

decreasing oxygen supply. Gas solubilities are inversely proportional to water temperature (Table 4.1) ; the saturation level for dissolved oxygen (DO) is reduced 50 percent with a water temperature increase from 32° F to 90° F; almost 0.1 mg/L per 1° F temperature rise. Water temperature increases have the same effect on a starem's dissolved oxygen resources as organic loadings from sewage treatment plants and results in lack of dissolved oxygen needed by microorganism for utilization of biodegradable wastes, and therefore may cause remarkable reduction in the self-purification capacity of a water body **(Zeller, 1970)**. Also temperature differences among various water bodies play a major role in the rate and extent of undesired algae growth, nutrient absorption, and general eutrophic processes that the growth of algae is one of the major causes of it **(Reis, 1972), (Krenkel and Novotny, 1980).** Temperature is also important because of its influence on water chemistry. The rate of chemical reactions generally increases at higher temperature, which in turn affects biological activity. It is useful to point out that Some compounds are also more toxic to aquatic life at higher temperatures **(Washington State Department of Ecology, 1991)**. Therefore, the effluent released from Khartoum Refinery is not suitable to be discharged into natural water bodies and streams with respect to its temperature. However, **(Reis, 1972)**, suggested that cooling ponds can be a relatively low cost and effective mode for waste heat treatment in petroleum refinery. The Relationship Between Temperature and Oxygen Solubility **(Washington State Department of Ecology, 1991)**, is shown in (Table 4.1) below.

**Table (4.1): The relationship between temperature and oxygen solubility**

| Temperature ($^o$C) | Oxygen solubility (mg/L) |
|---|---|
| 0 | 14.6 |
| 5 | 12.8 |
| 10 | 11.3 |
| 15 | 10.2 |
| 20 | 9.2 |
| 25 | 8.6 |
| 100 (Boiling) | 0 |

## 4.1.1.2 pH

This is the measurement of the hydrogen-ion concentration in the water or wastewater (with a decrease of one full unit representing an increase in acidity of ten times), and it can be affected by the presence of inorganics, organics, solids, and biological contaminants. It is a crucial water and wastewater quality parameter because wastewater reuse or discharge applications usually have restrictions on the acceptable pH range of the stream **(Zinkus et al., 1998)**. High pH values tend to facilitate the solubilization of ammonia . The precipitation of carbonate salts (marl) is encouraged when pH levels are high. Low pH levels tend to increase carbon dioxide and carbonic acid concentrations. Lethal effects of pH on aquatic life occur below pH 4.5 and above pH 9.5 **(RISC, 1998)** . Heavy metals such as cadmium, lead, and chromium dissolve more easily in more acidic water (lower pH). This is important because many heavy metals also become much more toxic when dissolved in water **(US EPA, 2012a)** The pH of the treated effluent was alkaline, fluctuated, and ranging from 7.9 in the second day to 9.45 in the first day, it was 8.07 in the third day (shown only the average in Table 4.2).

**Table(4.2): The physical quality of the MP effluents and comparison with National Sudanese standards and International standards.**

| Parameter | Unit | Result | MEM | WB/ IFC | OME | MEF | FEPA |
|---|---|---|---|---|---|---|---|
| Temperature increase | °C | 12* | – | $\leq 3$ | – | $\leq 5$ | Max.T: 30 |
| pH | – | 8.47* | $6-9$ | $6-9$ | $5.5-9$ | $6-8.5$ | $6.5-8.5$ |
| TS | mg/L | 314♦ | – | – | – | – | – |
| TDS | mg/L | 258♦ | – | – | – | – | 2000 |
| TSS | mg/L | 56♦ | – | 30 | 15 | 20 | 30 |
| Conductivity | µs/cm | 746.6♦ | – | – | – | – | 600 |
| Turbidity | NTU | 43.25* | – | – | – | – | 10 |

*Note*: *Average results for samples taken in three consecutive days; each is a composite of three grab samples at eight hours intervals per day, ♦ Results for three consecutive days composite samples,Max.T:Maximum temperature.

Despite the high pH value in the first day (9.45), which was above the National Sudanese standards and international standards limits of 6-9, the average value (8.47) fell within the local national , WB, and IFC limits of $6-9$ **(MEM, 2005)**, **(WB, 1998)**, and **(IFC, 2007)**, and marginally within India and Nigeria standard limits of $6-8.5$ **(MEF, 2008)** and **(FEPA, 1991)**. However, the average pH of the effluent is slightly higher than the FAO guidelines for irrigation water quality pH of 6.5-8 **(FAO, 1985)**. The result is higher than the findings of Uzoekwe and Oghosanine **(2011)**, Hamza *et al*.**, (2012)**, and Sharif **(2008)**. Uzoekwe and Oghosanine found that the pH mean value of the treated effluent to be 6.26; Hamza et al. who found almost neutral pH of 7.1 attributed this neutrality to the pH control chemicals (e.g slake lime) added; Sharif obtained an average pH value of 7.4 from Dora Refinery treated effluent, Iraq. According to de Brito **(2009)**, the effluent pH

measured for Lindsey, Eastham, Pembroke, Humber, and Grangemouth oil refineries in UK were 7.45, 6.84, 7.21, 7.71, and 7.35, respectively.

This relatively high pH value could be attributed to relatively inefficient pH control practiced through chemicals addition or insufficient neutralization of sour water and spent caustics in Khartoum Refinery. However the average pH value of Khartoum Refinery effluent from monitoring pond was exactly identical with the mean value of 8.47, of seven samples collected over a period of seven months, obtained by Otokunefor and Obiukwu **(2005)** from observation pond wastewater which is a combination of treated wastewater and non-processed wastewater in Kaduna Refinery, Nigeria.

### 4.1.1.3 Total dissolved solids (TDS)

Dissolved components are smaller than colloidal particles (about 0.1 micron) and are dispersed as individual molecules or ions throughout the solution (water) **(Zinkus *et al*., 1998)**.

The concentration of TDS of 258 mg/L (Table 4.2) in the composite sample was found relatively high enough to affect transparency as observed (field observation), but was satisfactory as it fell within the WHO **(2011)** specified limit of 1000 mg/L and of no degree of restriction on use for irrigation purposes, (<450 mg/L ) according to the FAO **(1985)** guidelines. TDS is not generally considered a primary pollutant (e.g. it is not deemed to be associated with health effects). It is used as an indication of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants.

### 4.1.1.4 Total suspended solids (TSS)

Unlike the other target pollutants, TSS is not a specific chemical. Instead, it represents a composite of all small particulates that are captured by a 0.45 micron filter during a specific analytical test. The test measures the presence of solids but does not identify the chemical nature of the solids. Suspended solids are particles,

whether mineral (e.g., soil particles) or organic (e.g., algae), that are larger than about 0.1 micron and that can be filtered from solution. Some suspended solids are of sufficient size and density to be settleable solids. Others that remain in suspension in a quiescent solution (e.g., colloids) are termed nonsettleable solids and are frequently measured with units of turbidity **(Zinkus *et al*., 1998)**.

High value of TSS (56 mg/L) was obtained from the analysis of the MP effluent composite sample (Table 4.2). This value exceeded the maximum allowable concentration in all the regulations guidelines used in this work. It was 1.9 times higher than the 30 mg/L of WB **(1998)**, IFC **(2007)**, and FEPA **(1991)** standard limits, 2.8 and 3.7 times higher than the standard limits of MEF **(2008)** of 20 mg/L and OME **(1992)** of 15 mg/L respectively. This high TSS in the effluent reflect inefficient TSS removal and may be a consequence of inadequate coagulation/sedimentation and floatation, separation, and filtration processes in the treatment plant of the refinery.

High concentrations of particulate matter affect light penetration and productivity, and habitat quality, and cause lakes and ponds to fill in faster. Particles also provide attachment places for other pollutants, notably metals and bacteria **(Washington State Department of Ecology, 1991)**. Furthermore, When the water is cloudy or turbid due to TSS and TDS content, sunlight will warm it more efficiently. This occurs because the suspended particles in the water absorb the sunlight which, in turn, warm the surrounding water. This leads to other problems associated with increased temperature levels **(US EPA, 2012b)**. High values of TDS and TSS must have contributed greatly to the low transparency of the effluent observed during samples collection.

### 4.1.1.5 Total solids (TS)

Total solids are dissolved solids plus suspended and settleable solids in water. Analytically the total solids content of a wastewater is defined as all the matter that remains as residue upon evaporation at 103 to 105 °C. Matter that has a significant vapor pressure at this temperature is lost during evaporation and is not defined as a solid.

A high concentration of total solids will make drinking water unpalatable, affect water clarity, and too high or too low levels can also reduce the efficiency of wastewater treatment plants, as well as the operation of industrial processes that use raw water **(US EPA, 2012c)**. However The value of total solids measured for the composite sample of three consecutive days grab samples was found to be 314 mg/L (Table 4.2). This value, although relatively high but, still within the regulations limits **(WHO, 2011)**.

### 4.1.1.6 Conductivity

Conductivity, or specific conductance, is a measure of the ability of water to conduct an electric current. It is sensitive to variations in dissolved solids, mostly mineral salts. In addition to being a rough indicator of mineral content when other methods cannot easily be used, conductivity can be measured to establish a pollution zone, e.g. around an effluent discharge **(Chapman, 1996)**. US EPA **(2012d)**, stated that Conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows. Streams that run through areas with granite bedrock tend to have lower conductivity because granite is composed of more inert materials that do not ionize (dissolve into ionic components) when washed into the water. On the other hand, streams that run through areas with clay soils tend to have higher conductivity because of the presence of materials that ionize when washed into the water. Ground water inflows can have the same effects depending on the bedrock they flow through.

Electrical conductivity of effluent samples is used in the present study, as an indicator of how salt free, ion free or impurity free the sample is. It is very important for the control of wastewater pollution level. The purer the water, the lower the conductivity. The high conductivity value which was recorded for the MP effluent sample (746.6 µS/cm) (Table 4.2), could be attributed to the use of inorganic chemicals in the refinery **(Rajasulochana *et al*., 2009)**, and dissolved ions in desalter stream generated from the crude desalting process. The conductivity value was higher than the FEPA **(1991)** standard limit of 600 µS /cm, and also higher than the WHO **(2011)** recommended value of 500 µS/cm. According to the FAO **(1985)** standard limits, the value fell within the category of slight to moderate degree of restriction on use for irrigation purposes (700-3000 µS/cm). The most influential water quality guideline on crop productivity is the water salinity hazard as measured by electrical conductivity (Ec). The primary effect of high Ec water on crop productivity is the inability of the plant to compete with ions in the soil solution for water a condition known as Osmotic drought (physiological drought). The higher the Ec, the less water is available to plants, even though the soil may appear wet. Because plants can only transpire "pure" water, usable plant water in the soil solution decreases dramatically as Ec increases .Water with Ec less than 250 µS/cm is considered good and that with greater than 750 µS/cm is unsuitable for irrigation **(Joshi *et al*., 2009)**. Studies of inland fresh waters indicate that streams supporting good mixed fisheries have a range between 150 and 500 µhos/cm. Conductivity outside this range could indicate that the water is not suitable for certain species of fish or macroinvertebrates **(US EPA, 2012d)**.

**4.1.1.7 Turbidity**

Turbidity is a measure of water clarity how much the material suspended in water decreases the passage of light through the water **(US EPA, 2012b).**

The turbidity values obtained for all the the three days were higher than WHO standards of 5 NTU **(WHO, 2011)**. They were 42.25, 55, and 32.5NTU

respectively (shown only the average in Table 4.2). The values ranged from 32.5 to 55 NTU with an average of 43.25 NTU which was higher than the WHO **(2011)** guidelines of 5 NTU for the discharge of wastewater into river or stream, and of 0.1 NTU for effective disinfection. Also the average turbidity exceeds the FEPA **(1991)** standard limit of 10 NTU. This high turbidity of the effluent could be affected by the high TSS content in the effluent, since TSS is highly contributing to turbidity value. Excessive turbidity in water/wastewater can cause problem for water purification/treatment processes such as flocculation and filtration which may increase treatment cost. High turbid waters are associated with microbial contamination **(Uzoekwe and Oghosanine, 2011)** . Turbidity causes decrease in photosynthesis process since turbidity precludes deep penetration of light in water **(Washington State Department of Ecology, 1991)**, leading to reduced production of dissolved oxygen (DO). Higher turbidity increases water temperatures because suspended particles absorb more heat. This, in turn, reduces the concentration of DO because warm water holds less DO than cold. Ultimately, the water receiving body is disqualified as source of water for domestic use in the community.

## 4.1.2 Inorganics

Table 4.3 shows the results of the inorganics quality analysis of MP effluent samples. From the results in the table, it is clear that all of the parameters were of high concentration levels, except for chloride and sulfate.

## 4.1.2.1 Alkalinity

The measurement of the capacity of water to neutralize acids is referred to as alkalinity **(US EPA, 2012e)**. The value of total alkalinity of a water body is very important in determining the ability of such water body to neutralize acidic pollution from wastewater, industrial effluents or rainfall. Alkalinity in wastewater results from the presence of the hydroxides, carbonates, and bicarbonates of elements such as calcium, magnesium, sodium, potassium, or ammonia. Of these, calcium and magnesium bicarbonates are most common. Borates, silicates, phosphates, and similar compounds can also contribute to the alkalinity.

**Table(4.3): The inorganics quality of the MP effluents and comparison with National Sudanese standards and International standards.**

| Parameter | Unit | Result | MEM | WB/ IFC | OME | MEF | FEPA |
|-----------|------|--------|-----|---------|-----|-----|------|
| Alkalinity | mg/L | 330$^\blacklozenge$ | − | − | − | − | − |
| Hardness | mg/L | 70.72* | − | − | − | − | 200 |
| Chloride | mg/L | 10.00$^\blacklozenge$ | − | − | − | − | 600 |
| Sulfate | mg/L | 58.30$^\blacklozenge$ | − | − | − | − | 500 |
| Cyanide | mg/L | 0.039$^\blacklozenge$ | − | 0.10 | 0.025 | 0.20 | < 0.01 |
| Sulfide | mg/L | 9.07* | 1.0 | 1.0 | − | 0.50 | 0.20 |

The alkalinity in wastewater helps to resist changes in pH caused by the addition of acids. The concentration of alkalinity in wastewater is important where chemical treatment is to be used, in biological nutrient removal, and where ammonia is to be removed by air stripping **(EEAA, 2002)**.

According to the UN Department of Technical Cooperation for Development **(1985)**, water having alkalinity up to 50 mg/L is considered to be weak alkaline, up to 100 mg/L is considered to be medium alkaline, while if the alkalinity is above 200 mg/L it is considered as strongly alkaline. On this basis it was observed that the effluent discharged from Khartoum Refinery was highly alkaline, having average total alkalinity of 330 mg/L in the MP effluent (Table 4.3). 100 mg/L was reported for alkalinity in the raw (untreated) effluent of Ennore refinery, India **(Rajasulochana *et al.*, 2009)**, and 90-170 mg/L for Mississauga Refinery

(Canada) Wastewater Treatment Plant **(Knight, 2014)**, respectively. According to **(Nazari *et al*., 2012)**, This highly alkaline effluent did not comply with the reclaimed water quality limitation(100-150 mg/l) for reuse in cooling towers in the refinery. The bicarbonate corresponding to obtained alkalinity value at the effluent pH will be more than 1.5 me/L, which means the effluent also fell within the degree of slight to moderate restriction on use for overhead sprinkling irrigation (1.5-8.5 me/L), according to the guidlines for interpretation of water quality for irrigation **(FAO, 1985)**.

### 4.1.2.2 Hardness

Hard water is usually defined as water, which contains a high concentration of calcium and magnesium ions. However, hardness can be caused by several other dissolved metals; those forms divalent or multivalent cations, including aluminum, barium, strontium, iron, zinc, and manganese. Normally, monovalent ions such as sodium and potassium do not cause hardness. These divalent cations have a propensity to come together with anions in the water to form stable salts. The type of anion found in these salts distinguishes between the two types of hardness, carbonate and non-carbonate hardness **(Sengupta, 2013)**. Carbonates, bicarbonates, and hydroxides contribute to carbonate hardness, whereas sulfates and chlorides are classified as non-carbonate hardness. Carbonate hardness is caused by the metals combined with a form of alkalinity; in contrast, non-carbonate hardness forms when metals combine with anything other than alkalinity. In the context of water use in industrial processes, however, and especially the reuse of treated wastewaters in a recycle and reuse system, the significance of hardness is in the scale-forming properties of calcium and magnesium salts **(Woodard, 2001)**. On the basis of hardness values water can be classified as 0–60 mg/L, soft; 61–120 mg/L, moderately hard; 121–180 mg/L, hard; and greater than as 180 mg/l very hard **( Sengupta, 2013)**.

Based on the above facts, in the present investigation, the MP effluents can be considered to be in the range of moderately hard, having an average hardness of 70.72mg/L and ranged from 68.05 to 72.06 mg/L (shown only the average in Table 4.3). The values of hardness reported during the study for three consecutive days samples (72.06, 68.05, and 72.06 mg/L) did not show much fluctuation. The average hardness in the MP effluent is below the maximum permissible limit of 500 mg/L set by the WHO **(2011)**, and lower than the values obtained by Uzoekwe et al. **(2011)** from Warri refinery treated effluent, Nigeria (103.38 mg/L), and Daflon et al. **(2015)** from Brazilian refinery(180 mg/L).

### 4.1.2.3 Chloride

Chloride is one of the major anions commonly found in ambient and wastewater. Excessive chloride in potable water is not particularly harmful and the criteria set for this anion are based primarily on palatability and its potentially high corrosiveness **(Lokhande *et al.*, 2011)**. Chloride in excess (> 250 mg/L) imparts a salty taste to water and people who are not accustomed to high chlorides may be subjected to laxative effects.

From the results of present investigation in Table 4.3, it was observed that the average chloride content in the MP effluent (10 mg/L) was clearly within the optimal level. This result idicates that the chloride content of the effluent was within the limits of 250 mg/L set by WHO **(2011)** and below the FEPA **(1991)** standard limit of 600 mg/L. This value is similar to that encountered in pristine freshwaters (< 10 mg/L) **(Chapman, 1996)**.

### 4.1.2.4 Sulfate

Sulphate is naturally present in surface waters as $SO_4^{2-}$. It is the stable, oxidised form of sulphur and is readily soluble in water (with the exception of lead, barium and strontium sulphates which precipitate). Sulphate can be used as an oxygen source by bacteria which convert it to hydrogen sulphide ($H_2S$, HS-) under anaerobic conditions **(Chapman, 1996)**. The sulfate ion is a major contributor to

salinity in many of the irrigation waters. Sulfate in irrigation water has fertility benefits, and most often irrigation water has enough sulfate for maximum production for most crops. Exceptions are sandy fields with <1 percent organic matter and <10 ppm $SO_4$-S in irrigation water **( Tak *et al.,* 2012)**.

The average value of sulfate in the effluent was found to be 58.3 mg/L (Table 4.3). The sources of sulfate ions in the effluent were sulfate salts and sulfuric acid used in the refinery processes, cooling tower blow down **(Iowa DNR, 2009)**, and Sulfur compounds that exist in almost all of the wastewater streams due to the presence of hydrogen sulfide, mercaptans and disulfides in the crude oil. Al Zarooni et al. **(2006)**, reported high concentration of sulfate in the treated sour water, in Al Ruwais Refinery (UAE), (up to 800 ppm), which is treated and then discharged to a corrugated plate interceptor (CPI), which separates the free oil from the wastewater, which is then sent to the final mixing pit where the wastewater is diluted with around 10,000m3/h of cooling water used in the refinery and finally disposed into the sea. However the average sulfate concentration in Khartoum Refinery MP was below permissible limit of 250 mg/L as specified by WHO **(2011)** and 500 mg/L set by FEPA **(1991)**, but it was 7.2 times higher than the mean sulfate concentration obtained by Nnabugwu **(2013)** who found the concentration to be 8.07 mg/L in the treated effluent of Nigerian National Petroleum Corporation (NNPC) Refinery at Alesa-Eleme near Port Harcourt, and about 4.2 times higher than the average sulfate concentration reported by Marcus and Ekpete **(2014)** from Port Harcort Refinery effluent also in Nigeria.

### 4.1.2.5 Cyanide

The presence of cyanide is a significant issue in industrial wastewater treatment and management. The complexity of the chemistry and toxicology of cyanide and the risk it poses in different environmental contexts make its management and remediation extremely challenging. Cyanide ion, $CN^-$, is probably the most important of the various inorganic species in wastewater. Cyanide, a deadly

poisonous substance, occurs in waters in ionic form or as weakly dissociated hydrocyanic acid at pH less than 8, which is more toxic to aquatic life than the free cyanide ion. In addition, it may occurs as complex compounds with metals. The form it takes is largely dependent on pH, temperature, dissolved oxygen, salinity, and the presence of other ions **(RISC, 1998)**. The toxicity of cyanides depends on their speciation; some ionic forms and hydrocyanic acid are highly toxic. Volatile HCN is very toxic and has been used in gas chamber executions in the United States **(Munter, 2003)**. The toxicity of complex compounds of cyanide depends on their stability. Weak complexes formed with metals such as zinc, lead and cadmium are extremely toxic. Copper complexes are less toxic, and cobalt and ferrous complexes are only weak toxicants **(Chapman, 1996)**.

Aquatic life's are killed by cyanide concentrations in the μg/l (part per billion) range, whereas bird and mammal deaths result from cyanide concentrations in the mg/L (part per million) range. Concentrations of free cyanide in the aquatic environment ranging from 5.0 to 7.2 μg/l reduce swimming performance and inhibit reproduction in many species of fish. Other adverse effects include delayed mortality, pathology, susceptibility to predation, disrupted respiration, osmoregulatory disturbances and altered growth patterns. According to US EPA **(1984)** Concentrations of 20 to 76 μg/l free cyanide cause the death of many species, and concentrations in over 200 μg/l are rapidly toxic to most species of fish. Invertebrates experience adverse non-lethal effects at 18 to 43 μg/l free cyanide, and lethal effects at 30 to 100 μg/l. Chronic cyanide exposure may affect reproduction, physiology, and levels of activity of many fish species, and may render the fishery resource non-viable. The sensitivity of aquatic organisms to cyanide is highly species specific, and is also affected by water pH, temperature and oxygen content, as well as the life stage and condition of the organism. Algae and macrophytes can tolerate much higher environmental concentrations of free cyanide than fish and invertebrates, and do not exhibit adverse effects below 160

µg/l or more. Aquatic plants are unaffected by cyanide at concentrations that are lethal to most species of freshwater fish and invertebrates **(Singare and Dhabarde, 2014)**. No significant correlation has been observed between toxicity of cyanide to fishes and alkalinity, hardness, or pH less than 8.3. However, Temperature and DO levels affected the toxicity of cyanide. The toxicity of cyanide increased with decreased DO levels below saturation. The tolerance of fishes to cyanide solutions that are increasingly lethal has been observed to decrease with a rise of temperature **(Pablo *et al.*, 1996)**.

The results of the present study reveals that the average cyanide content in the MP effluent was found to be 0.039 mg/L (Table 4.3). The observed value was very much above the maximum tolerable limit set by US EPA for freshwater aquatic life chronic criterion of 5.2 µg/L and for marine water of ≤1.0 µg/L **(US EPA, 1986)**. Also it was about 1.6 times above the OME **(1992)** standard limit of 0.025 mg/L and about 4 times above the FEPA **(1991)** standard limit of < 0.01 mg/L. However, it was within the permissible limits of the WHO **(2011)** of 0.07 mg/L, and of the WB **(1998)**/ IFC **(2007)** standard limit of 0.1 mg/L. The average cyanide content in the present work was about 12 times lower than effluent cyanide of Kaduna refinery (Nigeria) as reported by Lekwot et al. **(2012)** at the entry of river Romi, but was about 4 times higher than the average value of 0.01 mg/L recorded by Nnabugwu **( 2013)**, and the mean value (< 0.01 mg/L) obtained by Marcus and Ekpete **(2014)** for the effluent from the same refinery (Kaduna Refinery). It is important here, also to note that the observed cyanide value in the effluents discharged from Khartoum Refinery was very much higher (about 5 times) than the mean value of 0.008 mg/L observed by Nwaichi, et al. **(2013)** in the ffluents collected from Warri Refinery in Nigeria.

**4.1.2.6 sulfide**

Chemically, Sulfide is the most reduced species of sulfur. Sulfide ion ($S^{2-}$) in water exist in equilibrium with hydrosulfide ion ($HS^-$) and hydrogen sulfide ($H_2S$).

Hydrogen sulfide is a soluble, highly poisonous, gaseous compound having the characteristic odor of rotten eggs. It dissolves in water at 4000 mg/L at 20°C and one atmospheric pressure. Biologically it is an active compound that is found primarily as an anaerobic degradation product of both organic sulfur compounds and inorganic sulfates. Since sulfides are known constituents of petroleum refinery wastes, the anaerobic decomposition of sewage, sludge beds, and algae is a major source of hydrogen sulfide. Soluble sulfides in water react with hydrogen ions to form $HS^-$ and $H_2S$, the proportion of each depending on the pH. The toxicity of sulfides derives primarily from $H_2S$ rather than from the hydrosulfide ($HS^-$) or sulfide ($S^{2-}$) ions. $H_2S$ dissolves in water and dissociates according to the reactions:

$$H_2S \rightarrow HS^- + H^+ \quad and \quad HS^- \rightarrow S^{2-} + H^+$$

At pH 9 about 99% of the sulfide is in the form of $HS^-$, at pH 7 the sulfide is equally divided between $HS^-$ and $H_2S$; and at pH 5 about 99% of the sulfide is present as $H_2S$ **(US EPA, 1986)**. USEPA also stated that the degree of hazard exhibited by sulfide to aquatic animal life is dependent on the temperature, pH, and DO. When present in water, soluble sulfide salts can reduce pH; react with iron and other metals to cause black precipitates; cause odor problems; and can be toxic to aquatic life. To aquatic animal life, $H_2S$ is a highly toxic compound in very low concentrations and has been the cause of mass fish mortality in aquaculture systems. The threshold limit value for fresh or salt water fish is 0.5 mg/L **(Giwa *et al*., 2013)**. The toxicity of solutions of sulfides to fish increases as the pH value is lowered. Sulfides also chemically react with dissolved oxygen present in water, thereby lowering dissolved oxygen levels **(US EPA, 1974)**. Henshaw **(1990)** reported that sulfide has a high oxygen demand of 2 mol $O_2$/mol S and thus may cause significant depletion of oxygen in receiving waters.

In the petroleum refining industry, major sources of sulfide wastes are crude desalting, crude distillation and cracking processes. Sulfides cause corrosion, impair product quality, and shorten the useful catlyst life. They are removed by

caustic, diethanciamine, water or steam, or appear as sour condensate waters in these initial processing operations **(US EPA, 1974)**. Hydrogen sulfide is the main component of refinery sour waters and can cause corrosion problems in overhead systems of fractionation towers, in hydrocracker and hydrotreater effluent streams, in catalytic cracking units, in sour water stripping units, and, of course, in sulfur recovery units **(Duissenov, 2012)**. Hydrosulfide ($HS^-$) and sulfide ($S^{2-}$) typically are the most dominant sulfur compounds found in spent caustics with concentrations that may exceed 2–3 wt% **(de Graaff *et al.*, 2011)**.

Based on the above discussion and according to the results obtained from the investigations carried out for sulfide content, it was obvious that Khartoum Refinery liquid effluent is not qualified neither for discharge into water or soil environments nor for reuse in the refinery processes or cooling system or boilers. As can be seen from Table 4.3, the sulfide concentrations measured in MP effluent during the study for three consecutive days samples (24.4, 2.0, and 0.8 mg/L) showed clear fluctuation and averaged 9.07 mg/L (shown only the average). This high fluctuation reflects instability of crude processing as well as of WWTP process. However, this high average value is attributable to inefficient sulfur recovery in sulfur recovery unit, insufficient treatment of sour and spent caustic waters streams, and frequent occasions of poor treatment of the whole effluent at the WWTP. Henshaw **(1990)** reported that petroleum refineries convert liberated $H_2S$ in their processes to elemental sulfur (partial oxidation), and this is most commonly done by burning $H_2S$ to $SO_2$ with air, which is then reacted over a catalyst to yield $S^0$ and water. The author concluded that the accumulation of sulfates (complete oxidation) and thiosulfates in the reaction liquid leads to catalyst poisoning and consequentely lower elemental sulfur production, which means more $H_2S$ is available in the waste. The average sulfide level of 9.07 mg/L exceeded all of the standard limits used in the present study. It was more than 9 times higher than the standard limits of Sudanese Ministry of Energy and Mining **(MEM, 2005),**

and of the WB/ IFC **(WB, 1998)/(IFC, 2007)** , both of 1.0 mg/L. The value was also more than 18 times higher than the Indian standard limit of 0.5 mg/L **(MEF, 2008)** and more than 45 times higher than the Nigerian standard limit of 0.2 mg/L **(FEPA, 1991)**. The WHO maximum permissible limit for hydrogen sulfide is 0.1 mg/L **(WHO, 2011)**. This limit is also exceeded by sulfide level in  the samples collected from the MP, which was about 91 times above the standard limit. US EPA **(1986)** stated that water containing concentrations in excess of 0.002 mg/L undissociated $H_2S$, (i.e., 1/4,535 of sulfide concentration in Khartoum Refinery effluent), would constitute a long-term hazard to most fish and other aquatic wildlife. According to FAO **(1985)**, water having $H_2S$ concentration of more than 2 mg/L is considered of severe degree of restriction on use for irrigation purpose owing to its contribution to clogging problems in localized (drip) irrigation systems. On the other hand, when compared to results of similar international investigations of petroleum refineries effluents, liquid effluent of Khartoum Refinery was observed to contain the highest sulfide level. Abdulkarim and Embaby **(2006)** reported that sulfide was not detected in the final effluent of Ruwais Refinery (UAE) which is then discharged into sea. Wagner and Nicell **(2001)** reported sulfide levels of 4.4 and 2.2 mg/L in two samples obtained from downstream of a dissolved air flotation unit prior to biological treatment in a Canadian petroleum refinery. Sulfide levels of 0.01 and 0.12 mg/L were obtained by Otokunefor and Obiukwu **(2005)** from Port Harcourt Refinery effluents and Sharif **(2008)** from Dora Refinery respectively.

## 4.1.3 Nutrients

The results of nutrients quality investigation of Khartoum Refinery monitoring pond (MP) effluent are presented in Table (4.4). As this table indicates, most of the parameters exhibit low levels except for ammonia-nitogen.

**Table(4.4): The nutrients quality of the MP effluents and comparison with National Sudanese standards and International standards.**

| Parameter | Unit | Result | MEM | WB/ IFC | OME | MEF | FEPA |
|-----------|------|--------|-----|---------|-----|-----|------|
| $NH_3- N$ | mg/L | 83.17* | 15 | TN=10 | 10 | 15 | 0.20 |
| $NO_3-N$ | mg/L | 0.01♦ | – | – | – | 10 | 20 |
| $NO_2-N$ | mg/L | 0.0026♦ | – | – | – | – | – |
| $P_{ortho}$ | mg/L | 0.48* | – | – | – | – | – |
| $P_{total}$ | mg/L | 2.64* | – | 2.0 | – | 3.0 | 5.0 |

*TN: Total nitrogen*

### 4.1.3.1 Ammonia- nitrogen

Ammonia ,which is the most reduced inorganic form of nitrogen, is an important component of the nitrogen cycle and because it is oxidized in the environment by microorganisms (i.e., nitrification), it is a large source of available nitrogen in the environment. The complexity of the nitrogen cycle, various rate determining environmental conditions for nitrification (e.g., pH, temperature), and the physical behaviour of ammonia (e.g., volatilization, adsorption) make determining the fate of ammonia in the environment extremely complex **(CCME, 2010)**. In aqueous solution, un-ionised ammonia ($NH_3$) exists in equilibrium with the ionised ammonia ($NH_4^+$). The concentration of total ammonia (often expressed on the basis of nitrogen as total ammonia nitrogen or TAN) is the sum of $NH_4^+$ and $NH_3$ concentrations. It is total ammonia that is analytically measured in water samples. Environment Canada **(1999)** reported that the main factors that influence the equilibrium between un-ionized and ionized ammonia are pH and temperature, and

that raising pH by one unit can cause the un-ionized ammonia concentration to increase nearly tenfold, while a 5$^\text{o}$C temperature increase can cause an increase of 40-50%. According to Chpman **(1996)**, The concentration of un-ionised ammonia (UIA) is dependent on the temperature, pH and total ammonia concentration. The author also reported that ammonia forms complexes with several metal ions and may be adsorbed onto colloidal particles, suspended sediments and bed sediments, and that it may also be exchanged between sediments and the overlying water.

Ammonia is considered one of the most important pollutants in the aquatic environment not only because of its highly toxic nature, but also its ubiquity in surface water systems **(US EPA, 2013)**. "Eutrophication" is the enrichment of surface waters with plant nutrients. It is the process of change from one trophic state to a higher trophic state by the addition of nutrient **(FAO, 1996)**. Ammonia as a nitrogen pollutant is one of the contributors to eutrophication which stimulates the growth of algae blooms resulting in oxygen deficiency in surface waters, which in turn causes fish to die from lack of oxygen. Nitrification of ammonia in water yields nitrate and nitrite anions; the former species can be responsible for methemoglobinemia in human infants if the contaminated water is ingested **(ATSDR, 2004)**. Ammonia has been known to be toxic to aquatic organisms for a long time and, therefore, detrimental to the ecological balance of water bodies. US EPA **(2013)** reported that three factors: pH, temperature and, to a lesser extent, salinity, influence the fraction of $NH_3$ in water, consequently affecting the toxicity of ammonia in the aquatic environment. pH and temperature are positively correlated with the toxicity of ammonia, and salinity is inversely correlated. Plants are more tolerant of ammonia than animals, and invertebrates are more tolerant than fish. The Agency also reported that un-ionized ammonia (UIA) may cause toxicity to Nitrosomonas spp. and Nitrobacter spp. bacteria, inhibiting the nitrification process which can result in the increased accumulation of ammonia in the aquatic environment, thereby intensifying the toxicity to beneficial bacteria and

aquatic animals. In petroleum refinery, ammonia is formed from the nitrogen bearing components of crude oil and can be found throughout petroleum refineries in both the gaseous and aqueous forms. Aqueous ammonia is present in the sour water generated in the vacuum distillation unit and steam strippers or fractionators. In conclusion, it is commonly found in overhead condensates from distillation and cracking and from desalting **(US EPA, 1974)**. Nitrogen components in refinery effluents consist of organic nitrogen (non- biodegradable and particulate fractions), ammonia as a degradation product of biodegradable organic nitrogen and ammonia not removed by sour water stripper, nitrate as a product of nitification (biological ammonia oxidation), and lastly nitrite which is also a nitrification product ; typically very low in refinery effluent **(US EPA, 2004)**.

In light of the above discussion and consideration of the total ammonia concentration obtained by analysis of MP effluent, it can be seen that Khartoum Refinery effluent was poorly managed with respect to ammonia content, and that it may greatly harm the receiving environment. Total ammonia-nitrogen concentration was minimum (16.8 mg/L) on the third day composite sample and maximum (204.5 mg/L) on the first day composite sample, whereas concentration of 25.2 mg/L was obtained for the second day sample (shown only the average in Table 4.4). Since the most amount of nitrogen removal occurs in the biological treatment and clarifier units **(Kenari *et al.*, 2010)**, this result suggests poor performance of these units in the refinery. The average total ammonia-nitrogen concentration (83.17 mg/L) exceeded the local Sudanese standards **(MEM, 2005)** and Indian standards **(MEF, 2008)** both of 15 mg/L. The average value was about 8 times above the canadian guidelines of 10 mg/L **(OME, 1992)** and the WB/IFC guidelines of 10 mg/L **(WB, 1998/ IFC, 2007)** set for total nitrogen (not ammonia nitrogen only); the value was very much exceeding (415 times) the Nigerian standard limits of 0.2 mg/L **(FEPA, 1991)**. The average ammonia concentration was greatly exceeding the WHO threshold limit for odor of 1.5 mg/L **(WHO,**

**2011)** . The acute (1-hour average) and chronic aquatic life criteria for ammonia in freshwater at pH 7.0 and 20°C, 17 and 1.9 mg/L total ammonia **(US EPA, 2013)** respectively, were highly exceeded by the average total ammonia concentration in the present study. Applying EPA formulas used to derive un-ionized ammonia (UIA) fractions as a function of pH and temperature **(US EPA, 2013)**, it was observed that un-ionized ammonia-nitrogen concentrations were 162.477 (79.5%), 2.780 (11%), and 2.465 mg/L (14.7%) for the first, second, and third day respectively. The average un-ionized ammonia-nitrogen concentration was calculated to be 55.907 mg/L, which reveals a significant fact, that 67.2 % of the average total ammonia-nitrogen in Khartoum Refinery effluent is in the form of toxic ammonia (i.e., un-ionized), whereas 32.8 % is ionized ammonia. This phenomenon would be expected and well understood under conditions of elevated temperature and alkaline pH that characterize the effluent as previously reported in sections 4.1.1.1 and 4.1.1.2, respectively. Moreover this value of average un-ionized ammonia is very much above the recommended criteria level of 0.019 mg/L for the protection of freshwater aquatic life set by the Canadian Council of Ministers of the Environment **(CCME, 2010)**. On the other hand, the average total ammonia-nitrogen content of Khartoum Refinery effluent was observed to be higher than the average results obtained from various international refineries effluents reviewed in the present study, as obtained in mg/L by Nnabugwu **(2013)** (0.90), Otokunefor and Obiukwu **(2005)** (8.52), Wanger and Nicell **(2001)** (8.70), Abdulkarim and Embaby **(2006)** (0.90), Kenari et al. **(2010)** (15.6), Daflon et al. **(2015)** (0.70), and De Brito **(2009)** 3.36, 32.76, 0.939, 0.0, and 0.0 from five UK refineries effluents investigated by the auther namely; Lindsey, Eastham, Pembroke, Humber, and Grangemouth Refinery, respectively.

**4.1.3.2 Nitrate- nitrogen**

Because nitrogen is an essential building block in the synthesis of protein, nitrogen data will be required to evaluate the treatability of wastewater by biological processes. Much anthropogenic nitrogen is released into air, water and soil, causing

gacascade of problems for human health and the environment. Nitrate, which is the most oxidized form of nitrogen (N) present in the environment **(CCME, 2003)**, is in particular a health hazard because of its metabolic reduction to nitrites. Nitrate in surface and groundwater has been considered a primary cause of methemoglobinemia in infants, also known as "blue baby syndrome", and the formation of nitrosamines from reduced nitrate in the stomach has been suspected to cause cancer **(Rezaee *et al.*, 2012)**. In lakes, concentrations of nitrate in excess of 0.9 mg/L tend to stimulate algal growth and indicate possible eutrophic conditions **(Chapman, 1996)**. In New South Wales, Australia, the EPA **(1995)** states that "from an environmental perspective, nitrate is the most critical form of nitrogen. Its solubility, mobility and stability mean that it is readily leached to groundwaters, it has an active role in the eutrophication process and, in drinking water, it poses a threat to human and animal health".

In petroleum refineries, generally there are two sources of nitrogen; crude oil and amines used to remove hydrogen sulfide from gas to meet low sulfur fuel requirements. Most of nitrogen should be recovered through sour water strippers (ammonia, thiosulfate, or nitrogen gas) and amine regeneration/reuse, small amount goes to wastewater as ammonia or organic nitrogen as amines **(US EPA, 2004)**. As mentioned in the previous section, nitrates exist in refinery effluents as a product of nitrification (biological ammonia oxidation). However, the results of the present investigation of Khartoum Refinery MP effluent revealed that the average nitrate-nitrogen concentration is 0.01 mg/L (0.0443 mg/L as $NO_3^-$), (Table 4.4), which is much lower than the recommended criteria levels of 50 mg/L (as $NO_3^-$) set by the WHO for short- term exposure **(WHO, 2011)** and far below the maximum permissible limits of 10 and 20 mg/L in Indian **(MEF, 2008)** and Nigerian **(FEPA, 1991)** regulations for discharge into inland surface water, repectively, and canadian aquatic life freshwater criteria of 13 mg/L as $NO_3^-$ **(CCME, 2012)**. The effluent can be considered safe for use in agriculture, since its

nitrate content falls within the class of no restriction on use for irrigation (< 22 mg/L as $NO_3^-$ ) **(FAO, 1985)**. This low nitrate level in the effluent reflect decreased activity of nitrifire microorganism or improper nitrification conditions that result in poor conversion of ammonia to nitrate which exists in the effluent mainly through nitrification process as mentioned above ; at the same time the few nitrates resulting from poor nitrification met with increased denitrifire microorganism under unaerobic conditions resulting in this low nitrate level. It should also be noted that the poor nitrification of biological treatment of the effluent in WWTP is confirmed by the very high ammonia content as previously discussed in section 4.1.3.1 and lower nitrate content recorded above. Additional support to this comes from De Brito **(2009)** in his MSc research aiming at investigation of the nitrification process in full-scale oil refinery biological wastewater treatment plants using culture independent techniques. The author studied ammonia and nitrate concentrations in influents and effluents from five refineries in UK. He reported that nitrification was occurring in the Lindsey, Humber and Grangemouth reactors and total ammonia removal was achieved within a short period, and that nitrate concentrations found in the effluent from the Lindsey, Humber and Grangemouth reactors ranged from 0.19 up to 1.54 mM; by contrast, the author observed that ammonia was not removed from the influent in the Eastham and Pembroke reactors, and no nitrate was detected in their final effluents. However, the average nitrate concentration of the MP effluent was lower than 82 mg/L obtained by Daflon et al. **(2015)**, 1.05 mg/L obtained by Kenari et al. **(2010)**, 0.754 mg/L obtained by Otokunefor and Obiukwu **(2005)** and 1.64 mg/L obtained by Marcus and Ekpete **(2014)**.

### 4.1.3.3 Nitrite- nitrogen

Nitrite concentrations in freshwaters are usually very low, 0.001 mg/L $NO_2$-N, and rarely higher than 1 mg/L $NO_2$-N. High nitrite concentrations are generally indicative of industrial effluents and are often associated with unsatisfactory

microbiological quality of water **(Chapman, 1996)**. Nitrite is added to some industrial processes to inhibit corrosion **(Munter, 2003)** and as an intermediate product between ammonia and nitrate in nitrification process, sometimes occurs in quantity when depressed oxygen conditions permit **(US EPA, 1974)**. Under normal circumstances, the nitrite form of nitrogen will not be present in large quantities due to its rapid oxidation or conversion to nitrate.

The results of the MP effluent analyses revealed that the average nitrite-nitrogen was 0.0026 mg/L (0.0085 mg/L as $NO_2^-$), (Table 4.4), which is far below the tolerable limit of 3 mg/L (3 mg/L as $NO_2^-$) set by the WHO **(2011)**. This value was higher than the average value of 0.0002 mg/L reported by Kenari et al. **(2010)** from Tehran Refinery effluent. The main cause of this low nitrite concentration in the effluent, which can not be isolated from the reasons for low nitrate concentration discussed previously in section 4.1.3.2, could be the ineffective nitrification in the biological treatment unit, since ammonia is oxidized first to nitrite which in turn rapidly oxidized to nitrate. Based on the above the effluent can be considered safe for  discharge into the environment.

### 4.1.3.4 Phosphorus – total

The phosphorus content in natural waters is usually regulated by microorganisms, so there is a balance in the available phosphorus and ecosystem requirements. However, if phosphorus input exceeds the ecosystem consumption rate, the problem of increased phosphorus concentration appears. Excess of phosphorus stimulates algae growth in water bodies, which in its turn decreases oxygen concentration and leads to eutrophication of the surface water bodies as mentioned in section 4.1.3.1. For instance, Panasiuk **(2010)** reported that in the USA the water bodies that cannot be used for drinking, fishing, recreation, irrigation or industry purposes are impaired in the 60% of cases because of eutrophication. Phosphorus in wastewater exists in three main forms: organic phosphates (with -P-O-C- bonds), condensed inorganic polyphosphates (with -P-O-P- bonds), including both chain

bonded polyphosphates and cyclic-bonded metaphosphates, and inorganic orthophosphates $PO_4^{3-}$ ions (**Tomar, 1999**).

Various forms of phosphates find their way into refinery effluents. They range through several organic and inorganic species and are usually contributed by corrosion control chemicals. Plant cooling systems may contain 20 to 50 mg/l of phosphate ion **(US EPA, 1974)**. Since the forms of phosphorus in waters or industrial wastes are so varied, the term total phosphate has been used to indicate all the phosphate present in an analyzed sample regardless of the chemical form. The results of the present study indicates that total phosphorus ($P_{total}$ ) level was minimum (1.45 mg/L) in the third day sample and maximum (4.25 mg/L) in the second day sample, while in the first day sample $P_{total}$ concentration was found to be 2.22 mg/L with average value of 2.64 mg/L (shown only the average in Table 4.4). This value is higher than the IFC standard limit of 2 mg/L **(IFC, 2007)**, but below the Indian an Nigerian standard limits of 3 **(MEF, 2008)** and 5 **(FEPA, 1991)** mg/L, respectively. To control eutrophication, the US EPA has established a recommended limit of 0.05 mg/L for total phosphates in streams that enter lakes and 0.1 mg/L for total phosphorus in flowing waters **(US EPA, 1986)**, therefore phosphorus released in Khartoum Refinery effluent needs greater care. The average Ptotal was higher than the average value recorded by Nnabugwu **(2013)** of 1.74 mg/L, and that of (0-2 mg/L) obtained by Sharif **(2008)**.

**4.1.3.5 Phosphorus – ortho**

Orthophosphates are one of the most reactive forms of phosphate, which include the inorganic forms, such as $PO_4^{3-}$, $HPO_4^{2-}$, and $H_2PO_4^-$. Orthophosphate ($P_{ortho}$) is a readily available to the biological community and typically found in very low concentrations in unpolluted waters. Poly forms, which are used for treating boiler waters and in detergents, in water, they are transformed into orthophosphate and available for plant uptake **(Tomar, 1999)**. Dissolved phosphate, including orthophosphate, occurs in small concentrations in water because it has low

solubility, is readily taken up by biota, and adsorbs to metal oxides in soils **(US Geological Survey, 1999)**.

From the results of present investigation it was observed that $P_{ortho}$ content ranged between 0.057 for second day to 1.28 mg/L for first day sample, while 0.114 mg/L was recorded for the third day ; the average value of $P_{ortho}$ was 0.48 mg/L (shown only the average in Table 4.4), which is lower than the values reported by Nnabugwu **(2013)** (3.68 mg/L), Marcus and Ekpete **(2014) (**6.21 mg/L**)**, and Otokunefor and Obiukwu **(2005)** (6.21 mg/L).

### 4.1.4 Organics

The results of the MP effluent analyses for organic pollutants content (BOD, COD, Oil and grease, and Phenols) are presented in Table (4.5). Organic characteristics of the treated effluent did not comply with the permissible limits, except for oil and grease which comply with all, but not with Indian guidelines.

**Table(4.5): The organics quality of th MP effluents and comparison with National Sudanese standards and International standards.**

| Parameter | Unit | Result | MEM | WB/ IFC | OME | MEF | FEPA |
|-----------|------|--------|-----|---------|-----|-----|------|
| BOD5 | mg/L | 41.20* | 20 | 30 | − | 15 | 10 |
| COD | mg/L | 611.33* | 100 | 150 | 200 | 125 | 40 |
| Oil & G | mg/L | 7.96* | 10 | 10 | 10 | 5.0 | 10 |
| Phenols | mg/L | 39.72* | 0.50 | 0.20 | 0.02 | 0.35 | 0.50 |

## 4.1.4.1 Biochemical oxygen demand (BOD)

The biochemical oxygen demand (BOD) is an approximate measure of the amount of biochemically degradable organic matter present in a water sample **(Chapman, 1996)**. It is defined by the amount of oxygen required for the aerobic micro organisms present in the sample to oxidise the organic matter to a stable inorganic form over a period of 5- days. BOD values have been widely adopted as a measure of pollution effect. It is one of the most common measures of pollutant organic material in water and is used as a pollutional indicator for the petroleum refining industry. It is important here to note that BOD directly affects the amount of dissolved oxygen (DO) in water bodies. The greater the BOD, the more rapidly oxygen is depleted in the water. The consequences of high BOD are the same as those for low DO: aquatic organisms become stressed, suffocate, and die **(Lokhande *et al*., 2011)** .

According to US EPA **(1974)**, almost without exception, wastewaters from petroleum refineries exert a significant and sometimes major oxygen demand. The primary sources are soluble biodegradable hydrocarbons and inorganic sulfur compounds, crude distillation, catalytic cracking, and the product finishing operations, are the major contributors of $BOD_5$. In addition, the combination of small leaks and inadvertent losses that occur almost continuously throughout a complex refinery can become principal $BOD_5$ pollution sources.

The BOD values obtained in the present study was found to vary between minimum of 34.3 mg/L in the effluents collected in the second day to maximum of 49.6 mg/L in the first day effluent sample, while the third day sample measured 39.7 mg/L and average BOD value was 41.2 mg/L (shown only the average in Table 4.5). All the above BOD values were higher than 20, 30, 15, and 10 mg/L maximum limits set for petroleum refinery effluent discharge, by Sudanese **(MEM, 2005)**, WB/IFC **(WB, 1998/ IFC, 2007)**, Indian **(MEF, 2008)**, and Nigerian

**(FEPA, 1991)** environmental bodies, respectively. It was also observed that the average BOD level in Khartoum Refinery treated effluent, as compared to that in international refinery effluents, was 68.7, 7.8, 4.8, and 2.4 times higher than the average BOD levels reported by Nwaichi et al. **(2013)** (0.60 mg/L), Otokunefor and Obiukwu **(2005)** (5.28 mg/L), Daflon et al. **(2015)** (8.6 mg/L), and Sharif **(2008)** (17 mg/L), but it was lower than the average values recorded by Lekwot et al. **(2012)** (260 mg/L) and Sarkodie et al. **(2014)** (60 mg/L). The average BOD content in the present study was similar to the average value obtained by Nnabugwu **(2013)** (40 mg/L).

**4.1.4.2 Chemical oxygen demand (COD)**

Chemical oxygen demand (COD) provides a measure of the equivalent oxygen required to oxidize the materials present in a wastewater sample, under acid conditions with the aid of a strong chemical oxidant, such as potassium dischromate, and a catalyst (silver sulfate). One major advantage of the COD test is that the results are available normally in less than three hours. Thus, the COD test is a faster test by which to estimate the maximum oxygen exertion demand a waste can make on a stream. However, one major disadvantage is that the COD test does not differentiate between biodegradable and non-biodegradable organic material. In addition, the presence of inorganic reducing chemicals (sulfides, reducible metallic ions, etc.) and chlorides may interfere with the COD test. The biological treatment systems allow good organic matter degradation; however, inhibition problems may occur because of the presence of many recalcitrant and toxic hydrocarbons, as for example the phenols **(Nacheva, 2011)**.

Considering COD values and the average value given in Table 4.5, it is stated that the investigated effluents in the present study have high organic loads. COD ranged from 425 (3$^{rd}$ day) to 904 mg/L (2$^{nd}$ day), the first day measured 505 mg/L and the average COD level was 611.33 mg/L (shown only the average in Table 4.5). All of the observed values were higher than the Sudanese and international standard

limits. The average COD was more than 6 times higher than the Sudanese standard limit of 100 mg/L **(MEM, 2005)**, more than 15 times higher than the Nigerian standard limit of 40 mg/L **(FEPA, 1991)**, about 5 times higher than the Indian guidelines limit of 125 mg/L **(MEF, 2008)**, about 4 times higher than the WB/IFC guideline value of 150 mg/L **(WB, 1998/IFC, 2007)**, and about 4 times higher than the Canadian maximum permissible limit of 200 mg/L **(OME, 1992)**. On the other hand, from comparison point of view, average COD quality of Khartoum Refinery effluent is evidently ranked the least, since it was much higher than the average COD reported by Lekwot et al. **(2012)** (80 mg/L), Daflon et al. **(2015)** (112 mg/L), Sharif **(2008)** (86.4 mg/L), Nwaichi et al. **(2013)** (1.89 mg/L), Otokunefor and Obiukwu **(2005)** (26.68 mg/L), Sarkodie et al. **(2014)** (423 mg/L), and Nnabugwu **(2013)** (65 mg/L). Since it is a known phenomenon that COD methods do not recover specific organic compounds, which are difficult to oxidize or are resistant to chemical oxidation, one might expect actual organic load containing resistant toxic compounds to be higher than the obtained value. Therefore the very high COD content recorded in the present study could be attributed to very limited COD removal efficiency in the biological treatment plant, which may be traced to toxic non-biodegradable substances (e.g., phenols)  that caused bacteria to die **(Sponza, 2003)**, resulting in high effluent COD. However, generally, conventional biological treatment such as activated sludge (used in Khartoum Refinery) is only able to degrade below 1000 mg/L of COD. Thus, an alternative treatment or pre-treatment of the wastewater is required. There are many treatment options available for the removal of pollutants successfully such as stripping, carbon adsorption and membrane process. In conclusion, this effluent needs additional treatment before its final disposal, otherwise it could adversely impact the receiving environment owing to its toxic content.

### 4.1.4.3 Oil and grease (Oil & G)

The term "oil and grease" normally refers to chemicals, containing mainly aliphatic and aromatic hydrocarbons, derived from diverse sources ranging from crude

petroleum and industrial derivatives to edible oils and fats and their oleo-chemical derivatives. Due to lower biodegradability, the main contaminants of concern are oil and grease originating from petroleum (i.e., derived from fossil fuels) and their derivatives which have found wide industrial uses **(Tong *et al.,* 1999)**. Oily wastewater pollution is mainly manifested in the following aspects **(Yu *et al.,* 2013)**: (1) affecting drinking water and groundwater resources, endangering aquatic resources; (2) endangering human health; (3) atmospheric pollution; (4) affecting crop production; (5) destructing the natural landscape, and even probably because of coalescence of the oil burner safety issues that arise. According to US EPA **(1974)**, in the petroleum refining industry, oils, greases, various other hydrocarbons and some inorganic compounds will be included in the extraction procedure of Oil & G determination. The majority of material removed by the procedure in a refinery wastewater will, in most instances, be of a hydrocarbon nature. These hydrocarbons, predominately oil and grease type compounds, will make their presence felt in the COD, TOC, and usually the BOD tests where high test values will result. The Agency also stated that oxygen demand potential of Oil & G is only one of the detrimental effects exerted on water bodies by this class of compounds. Oil emulsions may adhere to the gills of fish or coat and destroy algae or other plankton. Deposition of oil in the bottom sediments can serve to exhibit normal benthic growths, thus interrupting the aquatic food chain. Soluble and emulsified materials ingested by fish maytaint the flavor of the fish flesh. Water soluble components may exert toxic action on fish. The water insoluble hydrocarbons and free floating emulsified oils in a wastewater will affect stream ecology by interfering with oxygen transfer, by damaging the plumage and coats of water animals and fowls, and by contributing taste and toxicity problems.

The oil and grease (Oil & G) content in the effluents collected from the MP was found to vary in the range of 2.3 ($2^{nd}$ day) to 15.2 mg/L ($1^{st}$ day), having the average concentration of 7.96 mg/L and a third- day sample concentration of 6.4

mg/L (shown only the average in Table 4.5). The average oil and grease content in the present study was below the standard limit of 10 mg/L set by Sudanese **(MEM, 2005)**, WB/ IFC **(WB, 1998/ IFC, 2007)**, Canadian **(OME, 1992)**, and Nigerian **(FEPA, 1991)** environmental authorities, but failed to comply with India standard limit of 5 mg/L **(MEF, 2008)**. The average Oil & G concentration was lower than 20.5 mg/L reported by Lekwot et al. **(2012)**, but was higher than 6.81, 5.9, and 4.27 mg/L obtained by Nnabugwu **(2013)** Sharif **(2008),** and Otokunefor and Obiukwu **(2005)**, respectively.

### 4.1.4.4 Phenols

Catalytic cracking, crude distillation, and product finishing and treating, are the major sources of phenolic compounds. Catalytic cracking produces phenols by the decomposition of multi cyclicaromatics , such as anthracene and phenanthrene. Some solvent refining processes use phenol as a solvent and although it is salvaged by recovery processes, losses are inevitable **(US EPA, 1982)**. Many phenolic compounds are more toxic than pure phenol ; their toxicity varies with the combinations and general nature of total wastes. The effect of combinations of different phenolic compounds is cumulative. Phenols and phenolic compounds are both acutely and chronically toxic to fish and other aquatic animals. Also, chlorophenols produce an unpleasat taste in fish flesh that destroys their recreational and commercial value **(US EPA, 1974)**. It is necessary to limit phenolic compounds in raw water used for drinking water supplies, as conventional treatment methods used by watersupply facilities do not remove phenols.

MP effluent quality analyses results revealed that the effluents sampled were violating the discharge limits in all the three- days sampling programme. The phenols content ranged between 37.78 (3rd day) and 41.53 mg/L (2nd day), and measured 39.85 mg/L in the first day sample (shown only the average in Table 4.5). The average value of 39.72 was largely exceeding the maximum permissible limits set by local and international authorities for petroleum refinery effluent

discharge, as it was more than 79 times higher than the local **(MEM, 2005)** and Nigeria **(FEPA, 1991)** standard limits of 0.5 mg/L, 198.6 times higher than the WB/ IFC **(WB, 1998/ IFC, 2007)** guideline value of 0.2 mg/L, 1,986 times higher than the Canadian **(OME, 1992)** maximum allowable limit of 0.02 mg/L, and 113.5 times higher than the Indian **(MEF, 2008)** maximum permissible limit of 0.35 mg/L. The value was also very much higher than the WHO maximum permissible limit of 0.2 mg/L **(WHO, 2011)**. Comparison with phenolics content of some international refineries effluents, depicts the mismanagement of phenolics effluents in Khartoum Refinery, where very much lower average phenols concentrations were reported by Abdulkarim and Embaby **(2006)** (not detected), Sharif **(2008)** (0.073 mg/L), Nnabugwu **(2013)** (0.14 mg/L), Otokunefor and Obiukwu **(2005)** (1.84 mg/L), and Nwaichi et al. **(2013)** (8.44 mg/L).

Besides causing serious damage to the environment and living beings, low concentration of phenol and phenolic compounds can inhibit the growth of microorganisms present in biological wastewater treatment systems, consequently promoting a significant reduction in the rate of degradation of contaminant compounds **( Silva, 2013)**. This explain the biological treatment failure in the present study, which was reflected in significantly high effluent concentrations of sulfide, ammonia, BOD, and COD as discussed previously in sections 4.1.2.6, 4.1.3.1, 4.1.4.1, and 4.1.4.2, repectively, and phenols, as mentioned above.

## 4.2  Oxidation Ponds Effluents Quality

The oxidation ponds at Khartoum refinery (Figures 3.2 and 3.3) are the final disposal terminals of treated wastewater discharged from the wastewater treatment plant (WWTP) through monitoring pond (MP). Effluent quality of the ponds was examined for different pollution parameters including: physical, inorganic, nutrient, organic, and heavy metals parameters. The concentrations of most environmentally significant pollutants previously investigated for MP effluent in section 4.1, in addition to selected heavy metals are also tested for oxidation ponds

effluent and the results are presented in Tables 4.6− 4.10. The physical, inorganic, nutrient, and organic parameters in oxidation ponds are compared to those in MP in figures 4.1−4.4. It is important here to note that Khartoum Refinery untreated effluents were bypassed from time to time and redirected to pond (C) instead of normal path where effluents are convoyed from MP through pipeline to pond (A) then pond (B) and lastly pond (C) (field observations).

## 4.2.1 Physical parameters

The results of the physical measurements are reported in Table (4.6) for pond (A), pond (B), and pond (C) . It can be seen from Table (4.6), that there were differences in the physical parameters levels among the ponds. These parameters will be discussed individually along with their levels in each pond in sections 4.2.1.1− 4.2.1.7.

### 4.2.1.1 Temperature

The WB **(1998)** stated that the effluent should result in a temperature increase of no more than 3° C at the edge of the zone where initial mixing and dilution take place, and where the zone is not defined, use 100 meters from the point of discharge, provided there are no sensitive ecosystems within this range. Therefore, the temperature was measured for pond (A) effluent only, which is considered the initial mixing zone because effluents from MP are received at this pond which discharge into pond (B) and then into pond (C). The temperature increase was found to be 6°C (Table 4.6), which is lower than the 12°C measured for MP effluent (Figure 4.1) because the effluent begins to cool or to aquire the ambient temperature as it moves along the distance between MP and oxidation ponds. The temperature increase was still above the standard limit set by the WB as mentioned above, and was also above the Indian standard limit of $\leq 5$°C. This increase could affect the physicochemical and biochemical processes in the oxidation ponds.

**Table (4.6): The physical quality of the oxidation ponds effluents and comparison with National Sudanese standards and International standards.**

| Parameter | Pond (A) | Pond (B) | Pond (C) | Ave. | MEM | WB/ IFC | OME | MEF | FEPA |
|---|---|---|---|---|---|---|---|---|---|
| Temperature increase (°C) | 6 | NA | NA | − | − | ≤ 3 | − | ≤ 5 | Max.T : 30 |
| pH | 10.90 | 10.15 | 8.62 | 9.89 | 6 − 9 | 6 − 9 | 5.5− 9.5 | 6 −8.5 | 6.5−8.5 |
| TS (mg/L) | 1083 | 1431 | 3841 | 2118.3 | − | − | − | − | − |
| TDS (mg/L) | 939 | 1329 | 3451 | 1906.3 | − | − | − | − | 2000 |
| TSS (mg/L) | 144 | 102 | 390 | 212 | − | 30 | 15 | 20 | 30 |
| Conductivity (µs/cm) | 1032 | 2361 | 5335 | 2909 | − | − | − | − | 600 |
| Turbidity (NTU) | 14.1 | 24.7 | 18.4 | 19.07 | − | − | − | − | 10 |

**4.2.1.2 pH**

The observed pH, presented in Table 4.6, was 10.9 in pond(A), 10.15 in pond (B), and 8.62 in pond (C) and the average pH was 9.89, which is above all the standard limits used in the present study, as well as higher than the MP effluent average pH (Figure 4.1). This increase in the pH could be attributed to photosynthesis and higher productivity in the oxidation ponds. Washington State Department of Ecology **(1991)** stated that Photosynthesis uses up hydrogen molecules, which causes the concentration of hydrogen ions to decrease and therefore the pH to increase. For this reason, pH may be higher during daylight hours and during the growing season, when photosynthesis is at a maximum. The Department also stated that when pollution results in higher productivity (e.g., from increased temperature or excess nutrients), pH levels increase, as allowed by the buffering capacity of the lake. It is important to note here that the higher pH values indicate that dissolved carbon dioxide was being utilized in algal photosynthesis, and increased temperature (discussed in section 4.2.1.1), might have enhanced the productivity of the ponds resulting in higher pH. The order of the pH was observed to be : pond (A) > pond (B) > pond (C), which indicates different productivity order and hence could suggest similar order for the fate of the other pollutants in the ponds.

**4.2.1.3 Total dissolved solids (TDS)**

Total dissolved solids were found to be 939, 1329, and 3451 mg/L in pond (A), pond (B), and pond (C), repectively, and averaged 1906.3 mg/L (Table 4.6), which is higher than the WHO standard limit of 1000 mg/L (WHO, 2011), and marginally within the group of slight to moderate degree of restriction on use for irrigation (450-2000) set by FAO **(FAO, 1985)**. Any slight increase in the TDS level could promote it to fall within the category of severe degree of restriction on use for irrigation ( > 2000 mg/L). The observed average TDS in oxidation ponds is more than 7 times higher than that obtained from MP (Figure 4.1).
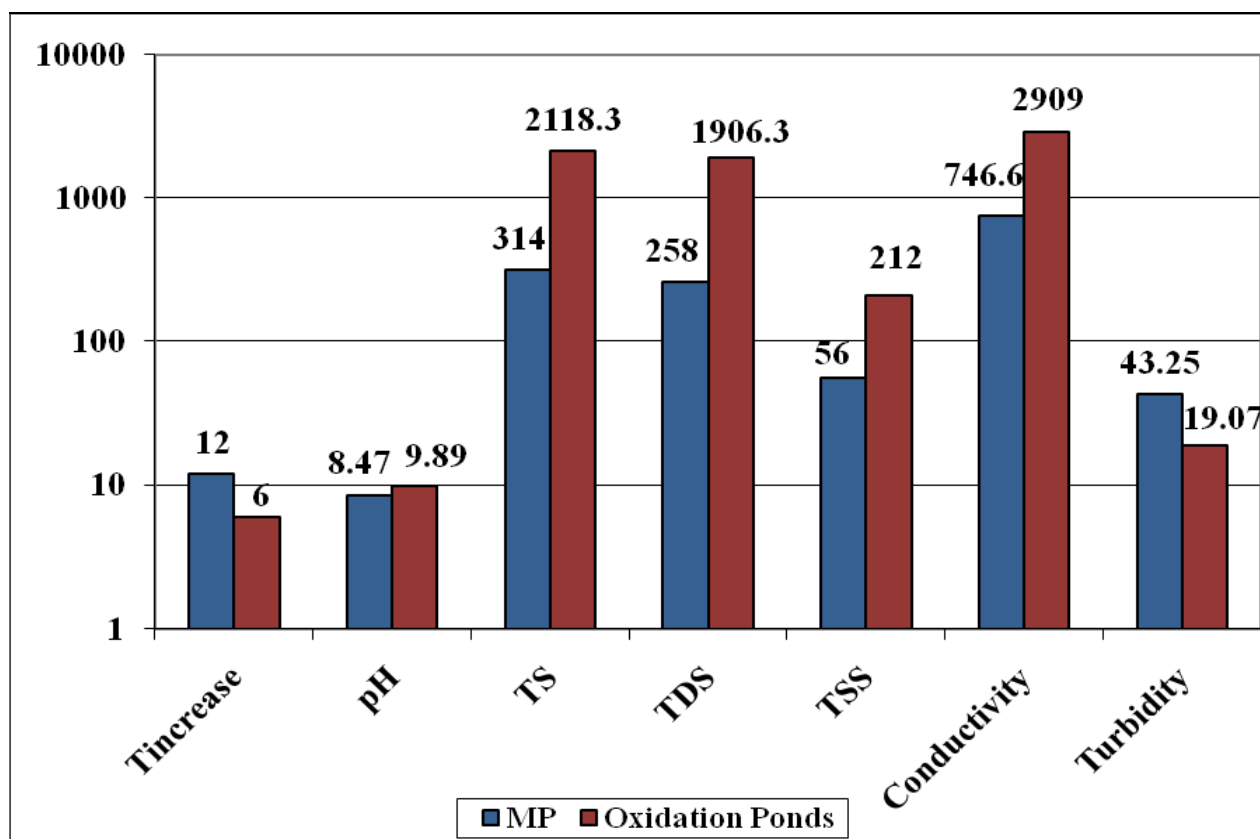
**Figure 4.1:** Comparison between the physical parameters levels in MP effluent and the oxidation ponds effluents

This high value could be attributed to accumulation of ions from influent wastewater (effluent from MP) such as chloride and sulfate in particular (higher chloride and sulfate discussion will follow), phosphate, nitrate, sodium, potassium, organic ions, and other ions, and to a lesser extent, calcium, magnesium, carbonate and bicarbonate ions owing to their low hardness and alkalinity as it follow in sections 4.2.2.1 and 4.2.2.2. Evaporation also may considered additional factor that could contribute to increased concentration. The order of TDS level was: pond (C) > pond (B) > pond (A).

**4.2.1.4 Total suspended solids (TSS)**

The maximum TSS level of 390 mg/L was observed in pond (C), the minimum of 102 mg/L in pond (B), 144 mg/L was observed in pond (A) and the average TSS was found to be 212 mg/L (Table 4.6). It was expected for TSS to decrease by

settling to the bottom sediment, but instead it was interestingly increased nearly 4 times TSS in MP (Figure 4.1). This could be traced to two reasons, one is physical and the other is biological; physically, sediment at the bottom of a body of water can be stirred up by shifting water flow and bottom-feeding animals resulting in more suspended matter depending on water depth and flow rate  and wind speed, biologically, warm temperatures, prolonged daylight, and release of nutrients from decomposition may cause algae blooms that increase TSS concentrations **(Washington State Department of Ecology 1991)**. The average TSS exceeded the maximum permissible limit of 30 mg/L set by WHO **(WHO, 2011)**.

**4.2.1.5 Total solids (TS)**

Total solids (Table 4.6) was maximum (3841 mg/L) in pond (C), minimum (1083 mg/L) in pond (A), intermediate (1431 mg/L) in pond (B), and averaged 2118.3 mg/L against 314 mg/L in the MP (Figure 4.1). This icreased TS is a consequence of of increased TSS and TDS values.

**4.2.1.6 Conductivity**

Conductivity, shown in Table 4.6, ranged from 1032  in pond (A) to 5335 µs/cm in pond (C), while it was 2361 µs/cm in pond (B). The average conductivity of 2909 µs/cm was about 4 times higher than MP effluent conductivity (Figure 4.1). Conductivity is directly related to the concentration of ions in the water, therefore this higher conductivity value may be due to increased TDS discussed previously in section 4.2.1.3. Oxidation ponds average conductivity suggest high salinity that can pose salinity hazard which affect crop productivity **(Tak *et al*.,  2012)**.

**4.2.1.7 Turbidity**

Lower turbidity levels (Table 4.6) were observed in pond (A) (14.1 NTU), pond (B) (24.7 NTU), pond (C) (18.4 NTU), and the average value was found to be 19.07 NTU. Oxidation ponds effluent turbidity was expected to be higher following the trend observed for TSS in the ponds, but in contrast a lower turbidity was observed ; it was only 44% of the MP effluent turbidity (Figure 4.1). The possible reason for this may lie behind the characteristics of the resuspended

sediment particles that contributed to high TSS levels, since turbidity is determined by the shape of particles, size distribution, refractive index, color and absorption spectra **(Omar and Jafri, 2013)**. In their study of the spectral reflectance of stream water characterized by heterogeneous TSS concentration and turbidity levels, Wu et al.**, (2014)** obtained low correlation coefficient between TSS and turbidity (0.24). The authors concluded that this low coefficient indicated that TSS was not the only variable to control the turbidity in the river water as measured by the optical technique, and that the COD was the other variable controlling the turbidity levels. Even though, the COD fraction clearly has less influence on the optical properties of the water, when compared with TSS. Another, but less probable reason for the lower turbidity obtained for oxidation ponds effluents, is that it may be before turbidity measurement, the coarse sediment particles, which have a short settling time is already settling down resulting in lower turbidity.

**4.2.2 Inorganics**

The results of the inorganic pollutants analyses are shown in Table (4.7) for pond (A), pond (B), and pond (C) . It can be observed from Table (4.7), that low levels of alkalinity, hardness, chloride, chromium (hexavalent), and sulfide, high levels of cyanide and sulfate are general characteristics of the ponds effluents. These parameters will be discussed individually along with their levels in each pond in sections 4.2.2.1−4.2.2.7.

**4.2.2.1 Alkalinity**

Alkalinity presented in Table 4.7, was highest in pond (B) (124 mg/L), lowest in pond (A) (69 mg/L), and of 92 mg/L in pond (C). The average alkalinity was obtained to be 95 mg/L against 330 mg/L in the MP effluent, which indicates 71.2% alkalinity removal (Figure 4.2). As mentioned previously in section 4.1.2.1, 95 mg/L means that oxidation ponds effluent is medium alkaline against strongly alkaline effluent in the MP. It is important to mention here that there was no detected hydroxide alkalinity in the effluent, while carbonate and bicarbonate were the dominating contributor to the total alkalinity.

**Table (4.7): The inorganics quality of the oxidation ponds effluents in( mg/L) and comparison with National Sudanese standards and International standards.**

| Parameter | Pond (A) | Pond (B) | Pond (C) | Ave. | MEM | WB/ IFC | OME | MEF | FEPA |
|---|---|---|---|---|---|---|---|---|---|
| Alkalinity | 69 | 124 | 92 | 95 | − | − | − | − | − |
| Hardness | 2.15 | 0.02 | 0.24 | 0.80 | − | − | − | − | 200 |
| Chloride | 46.3 | 248.6 | 48.8 | 114.57 | − | − | − | − | 600 |
| Sulfate | 30.6 | 3056 | 932 | 1339.5 | − | − | − | − | 500 |
| Cyanide | 0.050 | 0.015 | 0.060 | 0.042 | − | 0.10 | 0.025 | 0.20 | < 0.01 |
| Sulfide | 0.109 | 0.002 | 0.274 | 0.128 | 1.0 | 1.0 | − | 0.50 | 0.20 |
| Chromium (hexavalent) | 0.018 | 0.004 | 0.005 | 0.009 | − | 0.05 | 0.30 | 0.10 | < 0. 1 |

Carbonates and bicarbonates measured 28 and 96 mg/L, 32 and 60 mg/L, 20 and 49 mg/L for ponds A, B, and C, respectively (data not shown) ; the average carbonate is 26.7 mg/L, while the bicarbonate average concentration is 68.3 mg/L. Alkalinity lowering observed in oxidation ponds effluents can be explained as carbonates of calcium and magnesium (low hardness discussion follow) precipitated in the sedement.

**4.2.2.2 Hardness**

From the results of present investigation (Table 4.7) it was observed that hardness was minimum (0.02 mg/L) in pond (B) and maximum (2.15 mg/L) in pond (A), whereas pond (C) effluent hardness was 0.24 mg/L. Results also show that the average hardness of oxidation ponds effluents was very low measuring only 0.80 mg/L against 70.72 at the MP (Figure 4.2). This indicates about 99% of the influent hardness was removed in the oxidation ponds. As stated previously in section 4.1.2.2, effluent of 0.80 mg/L hardness considered very soft, moreover this high removal indicates that it was the carbonate (not non-carbonate) hardness who was responsible for the total hardness in the effluent. This is consistent with the lower alkalinity measured in oxidation ponds effluents as discussed previously in section 4.2.2.1. Based on the above discussion, the possible mechanism for hardness removal is that calcium and magnesium carbonates are precipitated in the pond sediment.

**4.2.2.3 Chloride**

The results (Table 4.7) revealed that chloride content of the oxidation ponds effluent was minimum (46.3 mg/L) in pond (A) and maximum (248.6 mg/L) in pond (B), whereas pond (C) effluent chloride content was 48.8 mg/L. Results also show that the average chloride content of oxidation ponds effluents was 114.57 mg/L, which is higher than that measured for MP effluent (10 mg/L) (Figure 4.2). This increased chloride level could be attributed to the continuous discharge from the refinery of effluents containing various chloride levels, besides dissolution of chloride salts in the ponds. This increase in chloride level could partly explain

corresponding increase in conductivity. Despite of this increase, however, chloride concentration is still below the maximum permissible limit of 250 mg/L set by the WHO **(WHO, 2011)**, and is not expected to cause chloride toxicity if used for surface irrigation as it measured 3.3 me/L (114.57 mg/L) within the category of no restriction on use for surface irrigation (< 4 me /L), but usage for sprinkler irrigation is questionable, since 3.3 me/L falls within category of slight to moderate restriction (> 3 me/L) **(FAO, 1985)**.
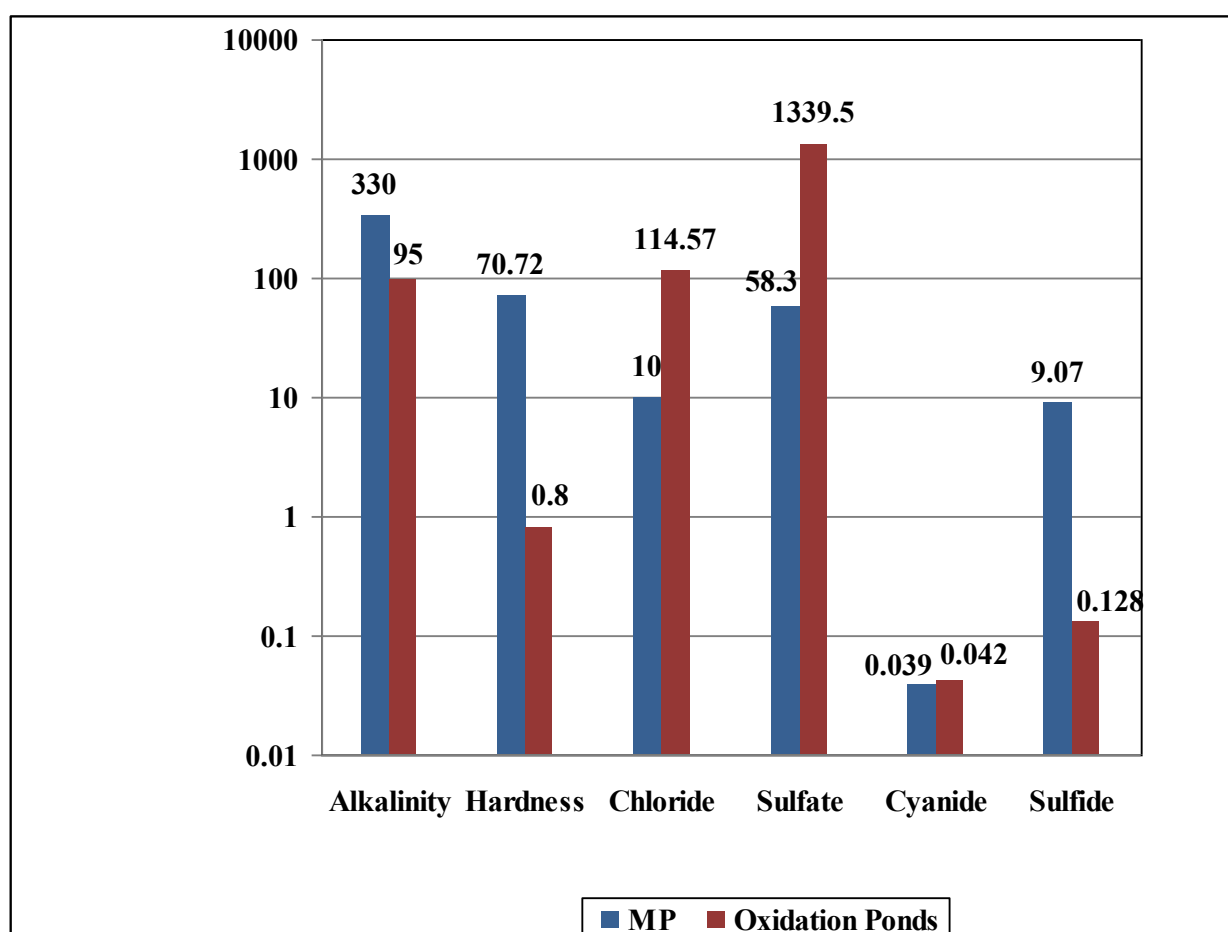


**Figure 4.2:** Comparison between inorganics levels in MP effluent and the oxidation ponds effluents.

**4.2.2.4 Sulfate**

Results of analyses of the oxidation ponds effluents (Table 4.7), showed that the effluent was highly contaminated with sulfate averaged 1339.5 mg/L. Sulfate level was fluctuating measuring minimum 30.6 mg/L in pond (A), maximum 3056 mg/L in pond (B), and declined to 932 mg/L in pond (C). The average sulfate concentration in oxidation ponds is about 16 times higher than that obtained in MP effluent (58.3 mg/L) (Figure 4.2). This is probably attributable to biological oxidation of sulfide and organic sulfur. Also oxidation of sulfide minerals (pyrite) could be another source. British Columbia Ministry of Environment **(BCME, 2013)** stated that, when sulphide minerals undergo weathering in the presence of water, the sulphide is oxidized to yield soluble sulphate ions. However, the average sulfate level exceeded the WHO standard limit of 250 mg/L **(WHO, 2011)**, and also above the FEPA standard limit for effluent discharge into inland water bodies of 500 mg/L **(FEPA, 1991)**. On the other hand, as mentioned previously in section 4.1.2.2 sulfate is a major contributor to salinity in irrigation water, therefore the oxidation ponds effluents may be not qualified enough for use in irrigation purposes. Contamination of groundwater through infiltration process also could be a possible impact. Apart from its direct effects, the observed high sulfate concentration in conjunction with increased chloride concentration (discussed previously in section 4.2.2.3), may give a satisfactory explanation for higher conductivity levels reported previously in section 4.2.1.6.

**4.2.2.5 Cyanide**

As can be seen from Table 4.7, cyanide concentration ranged from 0.015 mg/L in pond (B) to 0.06 mg/L in pond (C). Cyanide level was 0.05 mg/L in pond (A), and the average value was found to be 0.042 mg/L, which is higher than the average value recorded for MP effluent (0.039 mg/L) (Figure 4.2). This increase of about 7.7%, may be explained as increased non-volatile ionic cyanide fraction ($CN^-$) in oxidation ponds at pH 9.89, which is retained in the effluent leading to higher cyanide levels, whereas, HCN fraction dominates at the MP (pH 8.47);

volatilization of HCN reduces concentrations of free cyanide (HCN + CN⁻). The average cyanide concentration in oxidation ponds effluents was above the FEPA **(1991)** standard limit of 0.01 mg/L for discharge into inland water body, more than 10 times higher than the US EPA cyanide aquatic life criteria value of 0.004 mg/L for human consumption of water + organism **(US EPA, 2015)**, above the maximum tolerable limit set by US EPA for freshwater aquatic life chronic criterion of 5.2 μg/L and for marine water of ≤1.0 μg/L **(US EPA, 1986)**. but below the WHO maximum permissible limit of 0.07 mg/L **(WHO, 2011)**.

## 4.2.2.6 Sulfide

From the results presented in Table 4.7, it can be observed that the minimum sulfide level was 0.002 mg/L in pond (B), maximum of 0.274 mg/L in pond (C) and measured 0.109 mg/L in pond (A), while the average sulfide concentration was found to be 0.128 mg/L aginst 9.07 mg/L in MP effluent (Figure 4.2). This 98.6% removal efficiency could be partly attributed to sulfide precipitation as metal sulfides from the alkaline (pH 9.89) effluent in oxidation ponds. Altas and B¨uy¨ukg¨ung¨or **(2008)**, noted that Sulfide removal from petroleum refinery wastewater may occur by precipitation with metals present in wastewater, such as iron, chromium, copper, zinc, nickel or cadmium. Moreover, the authors after running their experiments concluded that increasing pH value of wastewater improved properties of flocculation and precipitation of sulfide as FeS. On the other hand, Considering the large increase in sulfate levels, as reported previously in section 4.2.2.4, the abundance of various sulfur compounds in such effluent, and naturally existing bacteria, one could add another and may be the main contributor to the observed sulfide removal efficiency ; it is the biological oxidation of sulfide and organic sulfur to sulfate that may greatly enhanced sulfide removal from the effluent. According to Henshaw **(1990),** Thiobacillus has been used successfully to treat sulfide-rich wastewaters from Soviet spas, with over 95% of the influent sulfide was converted to sulfate in an upflow reactor, where influent $H_2S$ concentrations of 20-60 mg/L were oxidised to less than 1 mg/L in the effluent.

Despite over 98 sulfide was removed, but the remaining levels could made the effluent unsafe for discharge into raw sources of domestic waters and may also be hazardous to aquatic life ; WHO standard limit for domestic water is 0.1 mg/L **(WHO, 2011)** and US EPA criteria for aquatic life is 0.002 mg/L **(US EPA, 1986)**.

### 4.2.2.7 Chromium (hexavalent)

As can be seen from Table 4.7, the minimum $Cr^{6+}$ level was 0.004 mg/L in pond (B), maximum of 0.018 mg/L in pond (A) and measured 0.005 mg/L in pond (C), while the average $Cr^{6+}$ concentration was found to be  0.009 mg/L, which is below the standard limits.

### 4.2.3 Nutrients

Nutrients concentrations in effluents samples collected from oxidation ponds are listed in Table (4.8). effluent samples collected from pond (A) contained higher levels of all the measured parameters (i.e. $NH_3$–N, $NO_3$–N, $NO_2$–N, $P_{ortho}$ and $P_{total}$), compared to the other ponds.

### 4.2.3.1 Ammonia-nitrogen

It was seen from Table 4.8, that ammonia was maximum of 14 mg/L in pond (A), minimum of 2.08 mg/L in pond (B), and of 2.28 mg/L in pond (C). The average ammonia concentration of 6.12 mg/L reveals 92.6% removal efficiency when compared to average ammonia concentration of 83.17 mg/L in MP effluent (Figure 4.3). This phenomenon can be partly explained by the reduction of the un-ionized ammonia fraction to nitrate by the action of nitrifying bacteria. Actually, nitrification favouring conditions are availble ;  un-ionized ammonia is dominating at the effluent pH of 9.89, oxidation ponds are naturally well aerated systems located in open area , besides the normal existence of nitrifying bacteria. According to US EPA **(1974)**, ammonia, in the presence of dissolved oxygen, is converted to nitrate ($NO_3^-$) by nitrifying bacteria with nitrite ($NO_2^-$) as an intermediate product.

**Table (4.8): The nutrients quality of the oxidation ponds effluents in( mg/L) and comparison with National Sudanese standards and International standards.**

| Parameter | Pond (A) | Pond (B) | Pond (C) | Ave. | MEM | WB/ IFC | OME | MEF | FEPA |
|---|---|---|---|---|---|---|---|---|---|
| $NH_3 - N$ | 14.00 | 2.08 | 2.28 | 6.12 | 15 | TN=10 | 10 | 15 | 0.20 |
| $NO_3 - N$ | 43.00 | 1.20 | 0.60 | 14.93 | – | – | – | 10 | 20 |
| $NO_2 - N$ | 1.24 | 0.16 | 0.036 | 0.479 | – | – | – | – | – |
| $P_{ortho}$ | 4.89 | 4.75 | 4.77 | 4.80 | – | – | – | – | – |
| $P_{total}$ | 6.43 | 5.93 | 5.78 | 6.05 | – | 2.0 | – | 3.0 | 5.0 |

From another view, the observed ammonia removal is probably attributable to ammonia volatilization, which, according to the Agency for Toxic Substances and Disease Registry **(ATSDR, 2004)**, is highly pH-dependent, and can also depend on other factors such as temperature, wind speed, and atmospheric ammonia concentration. Once again, favourable conditions are available ; high pH, effluent of increased temperature, and open space area. Although ammonia was greatly removed but not efficiently below the standard limit of 1.5 mg/L set by the WHO **(WHO, 2011)**, and the US EPA aquatic life criteria of 1.9 mg/L **(US EPA, 2013)**.
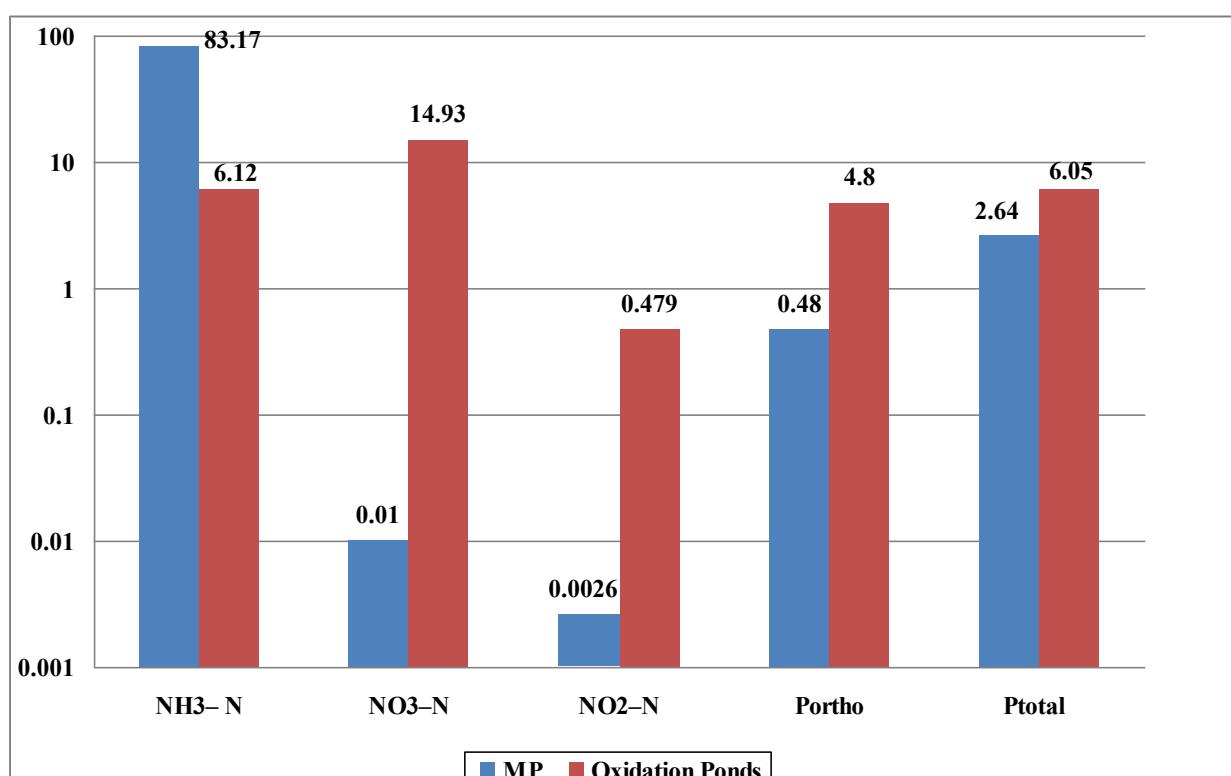


**Figure 4.3:** Comparison between nutrients levels in MP effluent and the oxidation ponds effluents.

### 4.2.3.2 Nitrate-nitrogen

It was observed from Table 4.8, that nitrate concentration (as N) in oxidation ponds effluents varied between 0.60 mg/L in pond (C) to 43 mg/L in pond (A). Pond (B) measured 1.2 mg/L, while the average nitrate concentration was obtained to be

14.93 mg/L (66 mg/ L as $NO_3^-$) against 0.01 mg/L from MP (Figure 4.3). Nitrate was 1,493 times higher due to nitrification of ammonia. This finding is in line with the results of ammonia determination recorded in the previous section. Although it is beneficial to remove ammonia, but not at the expense of safe nitrate levels. As mentioned previously in section 4.1.3.2, such high nitrate levels can cause eutrophication, toxic to fish and aquatic life, and would greatly threaten surface water and especially ground water. The average nitrate level in the oxidation ponds effluents is higher than the WHO standard limit of 50mg/L as $NO_3^-$ (**WHO, 2011)**, higher than the Indian standard limit of 10 mg/L as N **(MEF, 2008)** for discharge into inland waters, higher than the Canadian aquatic life criteria of 13 mg/L as $NO_3^-$ **(CCME, 2012**), and classified as slightly to moderately restricted on use for irrigation (5-30 mg/L as N) **(FAO, 1985)**. This alarming nitrate level can lead to contaminated groundwater through infiltration and percolation of effluents. Under the unaerobic conditions in the aquifer, nitrate is reduced to nitrite ; the former species can be responsible for methemoglobinemia in human infants if the contaminated water is ingested.

**4.2.3.3 Nitrite-nitrogen**

Results presented in Table 4.8 revealed nitrite-nitrogen levels of 0.036 mg/L in pond (C), 0.16 mg/L in pond (B), 1.24 mg/L in pond (A), and 0.479 mg/L as average value compared to 0.0026 mg/L in MP effluent (Figure 4.3). It was observed that average nitrite level in oxidation ponds was 184 times higher, probably due to nitrification of ammonia, since it is an intermediate product in the process, and could be formed in occations of depressed oxygen conditions near the bottom. If nitrite continued to increase it may contaminate the groundwater and adds to nitrite from reduced nitrate in the aquifer, where unaerobic conditions are dominant retaining this nitrite without oxidation to nitrate ; in this case, risk of methemoglobinemia in infants consuming this water is greater. Needless to say, the better the water quality at source, the lower the risk factors involved.

**4.2.3.4 Phosphorus – total**

It was seen from Table 4.8, that $P_{total}$ was maximum of 6.43 mg/L in pond (A), minimum of 5.78 mg/L in pond (C), and of 5.93 mg/L in pond (B). The average $P_{total}$ level of 6.05 mg/L was 2.3 times higher as compared to average concentration of 2.46 mg/L in MP effluent (Figure 4.3). This increase in P levels may be due to release from the sediment, which is, according to US EPA **(1973),** influenced by water and sediment composition and accelerated by temperature and the presence of a P sink such as an anion exchange resin or phytoblankton as a biological resin. The effluent pH of 9.89 can enhance P release **(Spivakov *et al.*, 1999)** from amorphous hydrated ferric oxides under anaerobic (reducing) conditions, to the overlying water column. Another source was reported by Spivakov et al. **(1999)**, who noted that, organic matter of allogenic or endogenic origin (structural elements of dead settling organisms) contain organic phosphate esters, which are hydrolysed by phosphatases and are a continuous source of phosphorus to the water column.

The average value of $P_{total}$ was higher than the IFC, Indian, and Nigerian standard limits of 2 mg/L **(IFC, 2007)**, 3 mg/L **(MEF, 2008)**, and 5 mg/L **(FEPA, 1991)**, respectively. Also the value exceeded the WHO maximum permissible limit of 5 mg/L (WHO, 2011), and the US EPA maximum recommended limits of 0.05 mg/L for total phosphates in streams that enter lakes and 0.1 mg/L for total phosphorus in flowing waters **(US EPA, 1986)**. It has to be mentioned here that the levels of phosphate in oxidation ponds effluents reported in this study, in addition to nitrate levels can cause eutrophication and may pose a problem if discharged into river or stream.

**4.2.3.5 Phosphorus – ortho**

The results of orthophosphate estimation in the oxidation ponds effluents outlined in Table 4.8, show a minimum value of 4.75 mg/L in pond (B), maximum value of 4.89 mg/L in pond (A), and of 4.77 mg/L in pond (C). The average value of 4.80 mg/L was 10 times higher than $P_{ortho}$ level of 0.48 mg/L at the MP (Figure 4.3). It

was observed that, increase of $P_{ortho}$ was more than 4 times the increase of $P_{total}$. This can be explain as inorganic P generally constituted the major portion of P released from sediments. This observation is similar to what observed by US EPA **(1973)** in a study conducted to investigate P release from lake sediment, where they concluded that seasonal changes in sediment P by release were most pronounced in the inorganic P fraction. The average is considered high when subjected to compliance standards concerning $P_{total}$ mentioned in the previous section.

### 4.2.4 Organics

The results of the organic parameters analyses are summarized in Table (4.9) for pond (A), pond (B), and pond (C) effluents . It is evident from the results that the (COD) values were high, while low contents can be seen for BOD, oil and grease and phenols.. Detail discussion of these parameters are provided in sectons 4.2.4.1−4.2.4.4 that follow.
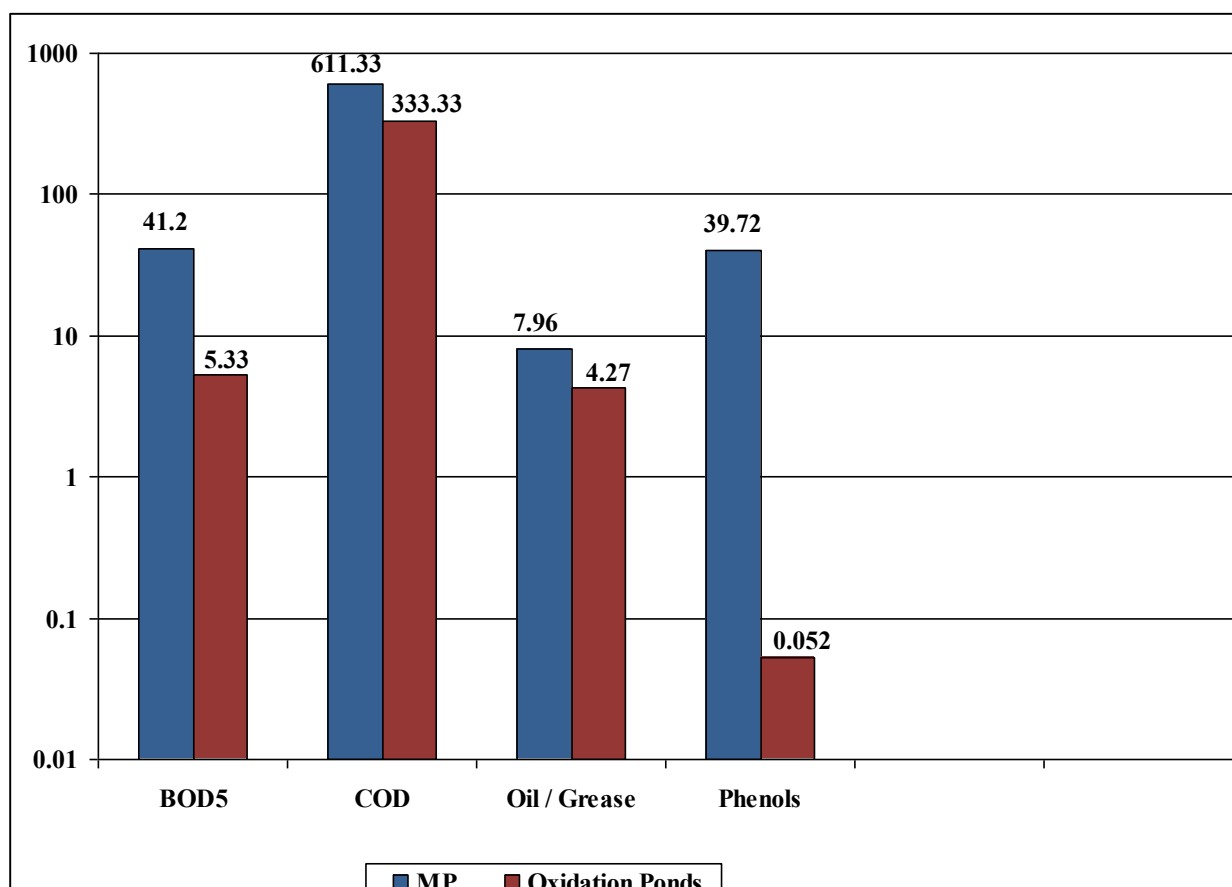
### 4.2.4.1 Biochemical oxygen demand (BOD)

As can be seen from Table 4.9, that BOD was minimum of 3 mg/L in pond (B), maximum of 8 mg/L in pond (A), , and of 5 mg/L in pond (C). The average BOD content of 5.33 mg/L demonstrates 87% removal efficiency when compared to average BOD of 41.2 mg/L in MP effluent (Figure 4.4). This is due to microbial biodegradation of the organic substances in the effluent, which is affected by microorganisms availability, aeration, temperature, pH, sufficient time, and BOD/COD ratio. The BOD/COD ratio is useful procedure for determining biodegradability in design and monitoring programs. A ratio above 0.4 indicates that effluent is readily biodegrated in activated sludge system and vice versa **(Sarathy, 2000)**. Based on the above, BOD/COD ratio of the MP effluent, which is the influent for the oxidation ponds, was calculated to be 0.067 indicating very low biodegradability, but because of the longer residence time, which was achieved by longer hydraulic retention times in oxidation ponds, metabolization of refractory substrates (i.e. a BOD/COD ratio less than 0.4) was possible resulting in the 87% biodegradation.

**Table (4.9): The organics quality of the oxidation ponds effluents in( mg/L) and comparison with National Sudanese standards and International standards.**

| Parameter | Pond (A) | Pond (B) | Pond (C) | Ave. | MEM | WB/ IFC | OME | MEF | FEPA |
|-----------|----------|----------|----------|------|-----|---------|-----|-----|------|
| $BOD_5$ | 8.00 | 3.00 | 5.00 | 5.33 | 20 | 30 | – | 15 | 10 |
| COD | 571 | 144 | 285 | 333.33 | 100 | 150 | 200 | 125 | 40 |
| Oil & G | 5.2 | 4.1 | 3.5 | 4.27 | 10 | 10 | 10 | 5.0 | 10 |
| Phenols | 0.069 | 0.039 | 0.049 | 0.052 | 0.50 | 0.20 | 0.02 | 0.35 | 0.50 |

The remaining BOD (5.33 mg/L) was not necessarily due to substrates initially present in the effluent. Sarathy (**2000)**, similarly obtained remaining BOD (7-16 mg/L) from Chevron Refinery wastewater biological treatment and attributed this to the accumulation of soluble microbial products.



**Figure 4.4:** Comparison between organics concentrations in MP effluent and the oxidation ponds effluents.

### 4.2.4.2 Chemical oxygen demand (COD)

From the results outlined in Table 4.9, it was observed that COD was minimum of 144 mg/L in pond (B), maximum of 571 mg/L in pond (A), , and of 285 mg/L in pond (C). The average COD concentration of 333.33 mg/L indicates only 45.47% removal efficiency when compared to average COD of 611.33 mg/L in MP effluent (Figure 4.4). COD removed at the refinery biological treatment unit was the easily biodegradable COD, that removed at the oxidation ponds (278 mg/L) was the

slowly biodegradable COD, while that remained (333.33 mg/L, i.e. the above average) is the residual COD. The residual COD measured in the present study, most probably was contributed by the non-biodegradable substances originally present in the effluent. Other studies on the biodegradation of refinery effluent reported similar residual CODs. For instance, **Sarathy (2000)**, obtained residual COD that varied from 104 mg/L to 116 mg/L and explained this as non-biodegradable compounds originally in the wastewater and a minor fraction resulting from the accumulation of soluble micobial products are responsible for the observed residual COD. However, the average COD was still above all the standard limits, which reflect the toxic nature of Khartoum Refinery liquid effluents. Moreover in oxidation ponds, the current very low BOD/COD ratio of 0.016 clearly indicates that the residual COD (333.33 mg/L) can not be further biodegraded and there is a need for treatment more efficient than biological treatment. The existence of toxic substances confirmed in the present study, would pose a great problem in the receiving environmental components.

### 4.2.4.3 Oil and grease (Oil & G)

The results of the assessment of Oil & G content in oxidation ponds effluents reported in Table 4.9, show a minimum value of 3.5 mg/L in pond (C), maximum value of 5.2 mg/L in pond (A), and of 4.1 mg/L in pond (B). It was observed that, the Oil & G content of the refinery effluent has been biodegraded in the oxidation ponds to an average value of 4.27 mg/L, corresponding to average value in the MP effluent of 7.96 mg/L (Figure 4.4), indicating 46.4% biodegradation. Biological treatment is generally effective in degrading dissolved oil and other types of stabilized emulsions which cannot be destabilized by coagulants. It is only effective on highly dilute oil-contaminated wastewaters **(US EPA, 1975)**. Other researchers studied the fate in the water envionment of oil and grease discharged from petroleum refineries. For instance, Knap and Williams **(1982)** in their investigation of the biological and physical fates of refinery effluent once discharged to Southampton Water estuary, found that most of the degradation takes

place in the lower molecular weight aliphatic fractions and that there was a specificity of removal throubh evaporation due to molecular weight, where evaporation was responsible for the removal of n-alkanes below carbon number 18. Also the authors investigated adsorption as another removal mechanism concluding that, the aliphatic fraction is adsorbed to the sediment particles at a much faster rate than is the aromatic fraction, and that the more water-soluble aromatic compounds would be adsorbed to the sediment to a lesser extent than the nonpolar aliphatic fraction due to their greater affinity for the aqeuous phase. However the oil and grease was brought to acceptable levels below local and international limits.

**4.2.4.4 Phenols**

Oxidation ponds effluents phenolic contents are summarized in Table 4.9. Results show that phenols concentration was minimum of 0.039 mg/L in pond (B), maximum of 0.069 mg/L in pond (A), and of 0.049 mg/L in pond (C). Average phenols concentration was found to be 0.052 mg/l against 39.72 mg/L in the MP effluent (Figure 4.4), which indicate removal efficiency over 99.8 % due to biodegradation and adsorption to sediment particles. The average value was below the local and international standard limits with the exception of the canadian standard limit of 0.02 mg/L.

**4.2.5 Heavy metals**

Several heavy metals ions may be found in refinery effluents. The major sources for their presence in wastewater are from the crude itself and corrosion products. The concentration of heavy metal ions varies considerably dependent upon the effectiveness of catalyst recovery in production process **(US EPA, 1974)**. Heavy metals are significant environmental pollutants, and their toxicity is a problem of increasing significance for ecological, evolutionary, nutritional and environmental reasons.

**Table (4.10): The heavy metals quality of the oxidation ponds effluents in( mg/L) and comparison with National Sudanese standards and International standards.**

| Element | Pond (A) | Pond (B) | Pond (C) | Ave. | MEM | WB/ IFC | OME | MEF | FEPA |
|---------|----------|----------|----------|------|-----|---------|-----|-----|------|
| Iron | 8.680 | 0.975 | 0.756 | 3.47 | − | 3 | − | 3 | 20 |
| Nickel | <0.100 | <0.100 | < 0.100 | < 0.100 | − | 0.5 | 1 | 1.0 | 1 |
| Copper | <0.030 | <0.030 | 0.051 | − | − | 0.5 | 1 | 1.0 | 1.5 |
| Zinc | 0.080 | 0.025 | 0.028 | 0.0443 | − | − | 1 | 5.00 | 1 |
| Chromium | <0.060 | <0.060 | < 0.060 | < 0.060 | − | 0.5 | 1 | 2.00 | 0.3 |
| Cadmium | <0.020 | <0.020 | <0.020 | <0.020 | − | − | − | 2.00 | < 0.01 |
| Lead | 0.110 | <0.100 | <0.100 | − | − | 0.1 | 0.1 | 0.10 | 0.05 |
| Barium | 0.240 | 0.220 | 0.560 | 0.34 | − | − | − | − | 1 |
| Selenium | <5.000 | <5.000 | <5.000 | <5.000 | − | − | − | 0.05 | 1 |
| Silver | <0.020 | <0.020 | <0.020 | <0.020 | − | − | − | − | 0.05 |

According to Nagajyoti et al. **(2010)** the term ''heavy metals'' refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration and in a general collective term, ''Heavy metals'', applies to the group of metals and metalloids with atomic density greater than 4 g/cm3, or 5 times or more, greater than water.

The results of the heavy metals analysis of oxidation ponds are presented in Table 4.10. The metals analysis result indicates slight increase in Fe and Pb. Fe concentration was minimum of 0.756 mg/L in pond (C), maximum of 8.680 mg/L in pond (A), of 0.975 mg/L in pond (B), and averaged 3.470 mg/L, which above the WHO/IFC and Indian standard limits of 3.0 mg/L **(WB, 1998/IFC, 2007)**, **(MEF, 2008)**, respectively. Also the observed average was above the WHO maximum permissible limit of 0.3 mg/L **(WHO, 2011)**, but below the FAO standard limit of 5 mg/L **(FAO, 1985)**. All Ni concentrations were < 0.100 mg/L, which is below the standard limits. Cu was maximum at pond (C) (0.051 mg/L), which is below the standard limits and measured <0.030 mg/L in both pond (A) and pond (B). Zn level was minimum of 0.025 mg/L in pond (B), maximum of 0.080 mg/L in pond (A), of 0.028 mg/L in pond (C), and averaged 0.0443 mg/L, which is below the standard limits. Total Cr measured < 0.060 mg/L in all the tested samples, which is below the standard limits. For Cd content, all the samples measured < 0.020. Pb concentration was maximum of 0.110 mg/L in pond (A), which is higher than the standard limits for petroleum refinery effluent discharge of 0.1 mg/L **(WB, 1998/IFC, 2007; OME, 1992; MEF, 2008)**, and above the Nigrian standard limit of 0.05 mg/L **(FEPA, 1991)**, and the WHO guideline value of 0.01 mg/L **(WHO, 2011)**. Minimum Ba concentration was found to be 0.220 mg/L in pond (B), maximum of 0.560 mg/L in pond (C), of 0.240 mg/L in pond (A), and averaged 0.340 mg/L, which is below the standard limits. Se and Ag were <5.000 and <0.020 mg/L in all samples, respectively. Ag cocentration was below the standard limits.

**4.3 Sediment Quality**

**4.3.1   Quality control**

Table 4.11 shows the results of the analysis of CRM IAEA-Soil-7 reference sample, that used in the validation of the analytical technique for total metals determination. The measured values of elements in the reference standard were comparable to the respective certified reference values. The percentage recovery of the elements ranged from 68 to 100%.

**Table (4.11): Total metal determinations in reference samples.**

| Element | Certified value (mg/kg) | Measured value (mg/kg) | % Recovery |
|---------|-------------------------|------------------------|------------|
| Ba | 159 | 141 | 89 |
| Cd | 1.3 | 1.3 | 100 |
| Cr | 60 | 52.9 | 88 |
| Cu | 11 | 7.5 | 68 |
| Fe | 25700 | 25600 | 100 |
| Ni | 26 | 23.8 | 92 |
| Pb | 60 | 59 | 98 |
| Zn | 104 | 96.4 | 93 |

**4.3.2 Heavy metals in oxidation ponds sediments**

The behaviour of metals in water bodies is a function of the substrate sediment composition, the suspended sediment composition, and the water chemistry. During their transport, the heavy metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena which affect their behaviour and bioavailability **(Singare *et al*., 2012)**. Sediments are the indicators of the presence of metals in an aquatic ecosystem. Because it eliminates metals from the water, accumulates and stores them over a long period,

even when the concentrations of metals in the water is low. For better understanding of ptential heavy metals impacts, their accumulation in the sediment and in water seem to be particularly important issues of present day research on impact assessments. The continuous discharge of effluents from Khartoum Refinery has prompted the researcher to carry the systematic study of pollution due to toxic heavy metals in sediments of the oxidation ponds, because they are located in an environmentally sensitive area.

The experimental data on the concentration (mg/kg) of the heavy metals Ag, Ba, Cd, Cr, Cu, Fe, Ni, Pb, and Zn in the sediment samples collected along sampling sites pond (A), pond (B), and pond (C) is presented in Table 4.12. From the results it was observed that, the range and average concentrations (mg/kg) were 0.20-2.80 (1.47) for Ag, 224.00 – 264.00 (247.33) for Ba, 0.20 – 2.78 (1.75) for Cd, 76.20 – 82.70 (79.83) for Cr, 27.90 – 527.60 (197.53) for Cu, 43950.00 – 54800.00 (48533.00) for Fe, 40.30 – 44.00 (41.73) for Ni, 13.00 - 14.00 (13.33) for Pb, and 106.20 – 189.00 (155.93) for Zn. Present study revealed that the order of heavy metals concentration in sediment was Fe > Ba > Cu >Zn > Cr > Ni > Pb > Cd > Ag, (Table 4.12).

High concentrations of Fe, Ba, Cu, Zn, Cr, and Ni may be related to alkaline nature of the ponds effluents, which was characterized by high pH. Metal mobilization in the sediment environment is dependent on physicochemical changes in the water at the sediment–water interface. The precipitation of lead, copper, chromium and zinc might be the result of alkaline pH in the form of insoluble hydroxides, oxides and carbonates. Metals such as chromium, copper and nickel have interacted with organic matter in the aqueous phase and settled, resulting in a high concentration of these metals in the sediment. The spatial distribution (Table 4.12), revealed that Pond (A) contained the maximum concentrations of Pb, Cd, and Ag, which may be precipitated hydroxides and

oxides of low solubility, and contained the minimum concentrations of Zn, Cr, and Ni, which were maximum in Pond (B), which in its turn was the minimum sink for Ba and Cu. Pond (C) shows high levels of Ba and exceptionally higher concentrations of Cu, probably due to bypass and accidental discharge of effluents.

Table(4.12): Total metal concentrations in sediment samples (in mg/kg dry weight).

| Element | Pond (A) | Pond (B) | Pond (C) | Average |
|---------|----------|----------|----------|---------|
| Ag | 2.80 | 1.40 | 0.20 | 1.47 |
| Ba | 254 | 224 | 264 | 247.33 |
| Cd | 2.78 | 2.26 | 0.20 | 1.75 |
| Cr | 76.2 | 82.7 | 80.60 | 79.83 |
| Cu | 37.1 | 27.9 | 527.6 | 197.53 |
| Fe | 43950 | 54800 | 46850 | 48533 |
| Ni | 40.3 | 44 | 40.9 | 41.73 |
| Pb | 14.0 | 13.0 | 13.0 | 13.33 |
| Zn | 106.2 | 189 | 172.6 | 155.93 |

As stated previously in section 4.2, Khartoum Refinery untreated effluents were bypassed from time to time and redirected to pond (C) instead of normal path where effluents are convoyed from MP through pipeline to pond (A) then pond (B) and lastly pond (C) (field observations). Accidental discharges of large quantities of pollutants can occur as a result of abnormal operation in a refinery and potentially pose a major local environmental hazard (WB, 1998). In fact, the exceptional trends in pond (C) was observed for other pollutants in the effluent

samples (eg., Ba, Cu, $S^{2-}$, $CN^-$, conductivity, TSS, TDS, and TS). The US Environmental Protection Agency (US EPA) has made sediment quality guidelines (SQGs) classifications (nonpolluted, moderately polluted, heavily polluted based on toxicity tests (reported in Pradit *et al*., **2009** and Sany *et al*., **2011**)). The concentrations of metals were compared with these sediment quality guidelines to assess environment condition and impact of Khartoum Refinery liquid effluent in this area. Assessing environmental and geochemical condition of metals in the sediment by comparison with US EPA SQGs (Table 4.13) show that Cr and Cu elements are categorized as heavily polluted, Ni and Zn are moderately polluted, Pb is unpolluted and Cd is at least not heavily polluted in the oxidation ponds sediments.

**Table (4.13): Comparison of average concentration of heavy metals obtained in this research with US EPA Sediment Quality Guidelines (in mg/kg dry weight).**

| Element | Not polluted | Moderately polluted | Heavily polluted | Present study |
|---------|--------------|---------------------|------------------|---------------|
| Ag | − | − | − | 1.47 |
| Ba | − | − | − | 247.33 |
| Cd | − | − | > 6 | 1.75 |
| Cr | < 25 | 25−75 | > 75 | 79.83 |
| Cu | < 25 | 25−50 | > 50 | 197.53 |
| Fe | − | − | − | 48533 |
| Ni | < 20 | 20−50 | > 50 | 41.73 |
| Pb | < 40 | 40−60 | > 60 | 13.33 |
| Zn | < 90 | 90−200 | > 200 | 155.93 |

There is a potential for significant soil, groundwater, and surface water contamination to have arisen at petroleum refineries and their surroundings.

According to Speight **(2006)**, such contamination consists of (1) petroleum hydrocarbons including lower boiling, very mobile fractions (paraffins, cycloparaffins, and volatile aromatics such as benzene, toluene, ethylbenzene, and xylenes) typically associated with gasoline and similar boiling range distillates, (2) middle distillate fractions (paraffins, cycloparaffins, and some polynuclear aromatics) associated with diesel, kerosene, and lower boiling fuel oil, which are also of significant mobility, (3) higher boiling distillates (long-chain paraffins, cycloparaffins, and polynuclear aromatics that are associated with lubricating oil and heavy fuel oil), (4) various organic compounds associated with petroleum hydrocarbons or produced during the refining process, for example, phenols, amines, amides, alcohols, organic acids, nitrogen and sulfur containing compounds, (5) other organic additives, for example, anti-freeze (glycols), alcohols, detergents, and various proprietary compounds, and (6) organic lead, associated with leaded gasoline and other heavy metals.

It was proved by experimental data in the present study that Khartoum Refinery effluent contains various types of physical, inorganic, nutrient, and organic pollutants. Also it was obvious that the effluent failed to comply with local and international regulations in terms of many pollution parameters in Mp and/or oxidation ponds effluents. Keeping this in mind and considering the topography, geology, and environmentally sensitive sites of the area mentioned erlier in section 1.12, one could conclude that the effluents generated from Khartoum Refinery could threaten the valuable environmental resources in the study area unless corrective actions are made. The area is sloping westward, where land elevation East of the refinery is about 564 m above sea level, at the oxidation ponds it is about 410 m above sea level, and it is reduced to 379 m above sea level at Wadramli village and its vicinal villages **(SGRA, 1997)**. As mentioned previously in section 1.6, The whole area is gently dipping westward with a number of shallow, dry wadis draining through the area from high ridges in the East of the

refinery towards the River Nile in the western part where the villages and the farms are located. The area is famous of its seasonal streams and frequently is affected by floods, see the map, (Figure 4.5), below. This means, during floods occations the polluted effluents could be leached and accumulate in the soils and farms, which opens the probability of accumulative effects associated with food chain and pose health risk to humans in the community area as well as far reach people who consume the products of these farms.
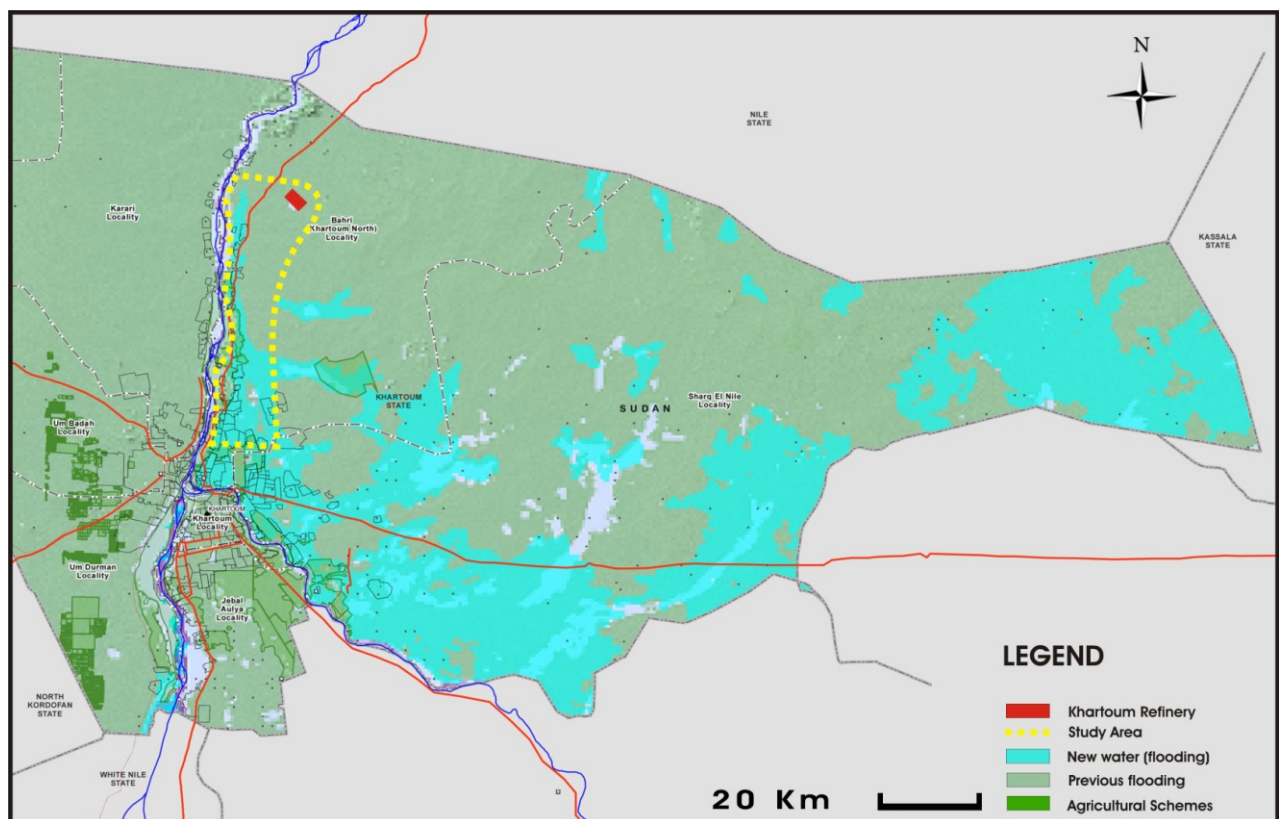


**Figure 4.5:** Khartoum State flooded areas. Source: United Nations Development Programme (UNDP), 2013.Khartoum, Sudan. Modified.

On the other hand, pollutants from the effluents may contaminate groundwater in the oxidation ponds area, where effluents are retaind there for many years. For instance, as reported in section 4.2.3.2 the average nitrate concentration of 66 mg/ L in oxidation ponds effluents exceeded the WHO maximum permissible limit and

may give rise to infants methemoglobinemia if they consume water with high nitrate levels. Another problem concerning the fate of heavy metals accumulated in the oxidation ponds sediments could occur if they are released, which is possible under flooding and heavy rains conditions. Sediment acts as a sink for pollutants. Environmental contaminants such as hydrocarbons and heavy metals have been known to have direct toxic effects when released into the aquatic environment **(Taiwo *et al*., 2012)**. Impacts to terrestrial ecosystems from the discharged effluents is another kind of adverse effects, which include a reduction or loss in total available habitat, destruction, or modification of food webs, and changes in populations **(Bahadori, 2014)**

# Chapter Five
## Conclusions and Recommendations

### 5.1 Conclusions

Refineries produce huge volumes of liquid effluents containing toxic substances such as heavy metals, hydrogen sulfide, phenols, ammonia, cyanide, and various types of hydrocarbons, resulting in local environmental impacts. Thus the effluent quality should be evaluated along with its environmental impact assessment because refineries are required to comply with the regulations set by the environmental authorized bodies, but this had not been coducted in Khartoum Refinery. There are critical gaps in knowledge with respect to the quality and environmental consequences of Khartoum Refinery liquid effluent. Therefore, this study had two main aims : to assess the quality of the final effluent discharged from Khartoum Petroleum Refinery and establishment of background base line data for pollution levels, and to assess the potential environmental impacts of the refinery effluents on the area. Based on the results of the study including sampling, laboratory investigations, and field survey and observations, the effluent quality and associated potential environmental impacts were assessed and discussed, and background data were established. The specific conclusions are listed below.

1. In this work it has been shown that the effluent in the monitoring pond (MP) was fluctuating and alkaline with average  pH 8.47. The levels of the physical parameters temperature increase (12°C), TSS (56 mg/L), conductivity (746.6 µs/cm), and turbidity (43.25 NTU), exceeded the maximum permissible limits. pH, TDS, and TS were within the standard limits.

2. The effluent was characterized by exceedingly high levels of sulfide (9.07 mg/L), suggesting inefficient management of sour water and caustic streams. Most of sulfide was expected to be in a form of ($S^{2-}$) ions, since the pH was

8.47. Also relatively high level of cyanide was measured (0.039 mg/L), exceeded some of the international standard limits and comply with others. Alkalinity, hardness, chlorides, and sulfates were within the recommended levels.

3. Interestingly high concentration of ammonia−nitrogen was observed (83.17 mg/L), reflecting poor nitrification in the biological treatment unit, and exceeded all the local and international standard limits. Since the proportions of un-ionized ammonia (UIA) and ionized ammonia are mainly dependent on pH and temperature, the toxic fraction (UIA) was calculated and found to be 55.907 mg/L as N, i.e., about 67.2 % of the total ammonia− nitrogen in the effluent. As a consequence of nitrification failure low nitrate and nitrite levels were remained in the effluent. Total phosphorus (2.64 mg/L) slightly exceeded some international standard limits and comply with others.

4. All of the organic parameters, except oil and grease, exceeded the local and international maximum permissible limits. They were 41.2, 611.33,and 39.72 mg/L, for BOD, COD, and phenols, respectively. The oil and grease (7.96 mg/L) was slightly below the local and some international standard limits, but above others.

5. The oxidation ponds effluents were also investigated to evaluate the efficiency of oxidation ponds in reducing pollution levels. The removal efficiencies of oxidation ponds were 50%, 55.9%, 71%, 98.9%, 98.6%, 92.6%, 87%, 45.46%, 46.4%, and 99.8% for temperature increase, turbidity, alkalinity, hardness, sulfide, ammonia, BOD, COD, oil/grease, and phenols, respectively. This reflects the biodegradation capability of the oxidation ponds and the adsorption capacity of their sediments. At the same time the low removal efficiencies of COD and oil/grease suggest toxic and recalcitrant componds in the effluent.

6. Despite the biodegradation capability of oxidation ponds mentioned above, it was obvious that, the levels of  many effective pollution parameters were

increasd. TS, TDS, TSS, conductivity, and chloride were increased by 574.6%, 638.9%, 278.6%, 289.6%, and 1,054.7%, respectively, probably due to resuspension phenomenon and dissolution of some salts. On the other hand, the pH increased by 16.8% (from 8.47 to 9.89 due to photosynthesis), and consequently cyanide was increased by 7.7%, attributable to increased non-volatile ionic cyanide fraction ($CN^-$). Sulfate was increased by 2,197.6% at the expense of high sulfide concentration influent to oxidation ponds through the action of sulfur oxidizing bacteria utilizing inorganic sulfide and organic sulfur compounds. As a result of ammonia nitrification nitrate and nitrite levels were increased by 149,200% and 18,323%, respectively, while ortho phosphate and total phosphorus were increased by 900% and 129.2%, respectively, probably attributable to phosphorus release from the sediments, which was enhanced by temperature and high pH of the oxidation oxidation ponds effluents.

7. In an effort to evaluate the pollution and fate of heavy metals, oxidation ponds were investigated in both effluents and sediments. The investigation, again showed the adsorption phenomenon, which is represented by the low concentrations of the metals in the water column and the corresponding high levels in the sediment. The assessment of the environmental and geochemical condition of metals in the sediment according to the US EPA sediment quality guidlines (SQGs) show that Cr and Cu elements are categorized as heavily polluted, Ni and Zn are moderately polluted, Pb is unpolluted and Cd is at least not heavily polluted in the oxidation ponds sediments.

**Recommendations For Future Research**

There are several aspects of this petroleum refinery liquid effluent research that have not been resolved in the present study. Some issues that warrant further studies include:

- The field sample study in **Chapter 4**, found the MP effluent to contain alkaline pH, and significantly high concentrations of TSS, Turbidity, sulfide, ammonia, BOD, COD, and phenols which were all above the standard limits, besides relatively high levels of conductivity, cyanide, total phosphorus, and oil and grease. The detailed and actual reasons behind this low quality were not closely investigated in this study. A closer step by step examination of the effluent streams befor reaching the MP may be interesting.

- MP effluent study in **Chapter 4**, showed high levels of BOD and COD exceeding the local and international standard limits and relatively high load of oil and grease. The organic load was studied collectively as BOD, COD, and oil and grease in this work. Detailed examination of individual organic pollutants and especially toxic recalcitrant hdrocarbons in the effluent will increase the knowledge and raise the awareness.

- From the results in **Chapter 4**, it seems that certain parameters such as pH, ammonia, BOD, COD, oil and grease, and phenols, exhibited a direct relation. A correlative study might be usefull in controlling these pollution parameters.

- Oxidation ponds sediments were investigated for heavy metals only and the results showed clear metals adsorption on the sediment. Investigation of the hydrocarbons accumulation in the sediment will help in assessing the fate of these toxic compounds.

- Heavy metals were investigated in the sediments as total concentrations in this work. Speciation study of heavy metals in the sediment will help to know their geochemical forms and bioavailability, consequently give important

informations about their fate and the hazard that they can pose to the surrounding environment.

• The present study was oriented to study the effluent quality and to make scientific predictions of the potential impact on the environment depending on geographic, topographic, geological, and statistical data of the area, but the actual impacts were not measured due to the recent operation of the refinery at the time of the study. Now the refinery has been operating for many years, therefore it is the suitable time to conduct a study on actual impact assessment by measuring pollution parameters in the soils, plants, animals, surface waters, and groundwaters in the vicinity of Khartoum Refinery.

• Excellent effluent water qualities can be produced from filtration and granular activated carbon adsorption treatment. Therefore, it is strongly recommended to construct an advanced treatment plant at Khartoum Refinery.

• Nowadays water conservation and pollution abatement are needed to provide increasingly higher levels of treatment for petroleum refinery wastewaters. Reducing treatment costs and the international goal of zero discharge of pollutants to the waterways give the incentive to minimize the volume of wastewater effluent. Therefore, the effluent from the recommended advanced treatment plant can be satisfactorily employed for cooling tower water, also the feed of manufacturing process water and boiler water supply. A study on reuse of Khartoum Refinery effluent is very important issue, because it would solve the problems of effluent quality and disposal method.

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