EFFECT OF HEAVY METAL FROM PETROCHEMICAL REFINERY ON THE SURFACE WATER AND SOIL

BY

UGWUOKPE EKENE DARLINGTON

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BEING A FINAL YEAR PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF ENGINEERING (B.ENG.) DEGREE IN AGRICULTURAL AND BIORESOURCES ENGINEERING.

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DECLARATION

I hereby declare that this project is a record of a research work that was undertaken and written by me. It has not been presented before for any degree or diploma or certificate at any University or institution. Information derived from personal communications, published and unpublished work were duly referenced in the text.

.... 18/02/2010

UGWUOKPE EKENE DARLINGTON **DATE**

CERTIFICATION

This project entitled "Effect of Heavy Metal From Petrochemical Refinery on the Surface Water and Soil: Case Study of Kaduna Refinery" by Ugwuokpe, Ekene Darlington, meets the regulations governing the award of the degree of Bachelor of Engineering (B.ENG.) of the Federal University of Technology, Minna, and it is approved for its contribution to scientific knowledge and literary presentation.

Mr. John .J. Musa
Supervisor

16/02/10
Date

Engr. Dr.A. A. Balami
H.O.D, Agricultural and Bioresources Engineering

17/02/10
Date

Engr. Prof. G. O. Chukwuma
External Examiner

10-02-10
Date

DEDICATION

This project work is dedicated to Almighty God who in his infinite mercy makes it possible for me to successfully complete my degree program in the Federal University of Technology Minna. And to my Gentle father, who took the giant step supporting, encouraging and financing my educational career.

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ABSTRACT

Heavy Metals are chemical elements, common to all kinds of soils, and their abundance ranks between percentage (Fe only) and parts per million. The very low general level of their content in soils and plants, as well as the biological role of most of these chemical elements, has led to them being grouped under the generic name of "microelements". When the soil has very high contents of such chemical elements, the term "Heavy metal pollution" is used. Heavy metal which is the subject of this project work are micro element which can be found in refinery waste water over the years. The quality and quantity analysis of this waste water was carried out and they were both found to be satisfactory. Copper was analyzed to be 0.09, 0.07, 0.10 respectively. This is within the specified range of 0 – 0.5 according to food and agricultural organization.

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ABBREVIATIONS OR SYMBOLS OR NOTATIONS

Ca	Calcium
Cr	Chromium
Cu	Copper
EDTA	Ethylene diamine tetra acetic acid
Ec	Electrical Conductivity
ds/m	Decisiemen per litre
FAO	Food and Agricultural Organization
Fe	Iron
Fe^{2+}	Iron(2)ion
Fe^{3+}	Iron(3)ion
H_2SO_4	Tetraoxosulphate VI acid
KRPC	Kaduna Refinery and Petrochemical Company
Mn	Manganese
Pb	Lead
S.S	Suspended solids
T.D.S	Total Dissolved Solids

CHAPTER ONE

1.0 INTRODUCTION

Kaduna refinery and petrochemical company is a subsidiary of NNPC occupying an area of 2.89km^2 South of Kachia Road. It is the largest combined refinery and petrochemical industry in the country. Its primary function is the refining of crude oil and the production of some petrochemicals. The plant have a refining capacity of 110, 000 barrels per stream day. Two types of crude oils are processed: 60,000 barrels per stream day of gulf oil crude from Escravolos (local crude) and 50,000 barrels per stream day of paraffin base crude oil imported from Venezuela, Kuwait and/or Saudi Arabia (foreign crude).

The petrochemical plant runs by Kaduna refinery and petrochemical company (KRPC) is designed to produce 30,000 mega tone per year of linear alkyl benzene suitable for processing into biodegradable detergents. Feed stocks for the process include kerosene, hydrogen – rich gas from the refinery and benzene from the benzene unit of the petrochemical plant. Production of linear alkyl benzene is via chain of processes. Besides linear alkyl benzene, there are secondary products such as kerosene, raffinate, heavy alkylates, solvents, heavy extracts and acid soluble oils. From this and many other petroleum – processing industries spread all over the nation, a large amount of wastes is being discharged, emitted and discarded daily to the environment.

1.1 BACKGROUND TO THE STUDY

The disposal of wastewater in most cities was carried out by the easiest method possible, without much regard to unpleasant conditions produced at the place of disposal. Irrigation, practiced in ancient Athens, was probably was the earliest method adopted by most municipalities. Problems arose when household wasted were admitted to storm sewers because the purification capacity of the watercourse into which they drained was often exceeded. Although the collection of wastewater dates from ancient times, the treatment of wastewater is a comparatively recent development dating from the late 1800s and early 1900s. As a result, separate sewers were built and wastewater treatment instituted. (Metcalf and Eddy, 2000)

1.2 STATEMENT OF THE PROBLEMS

Wastewater is objectionable in appearance and extremely hazardous in content due to the number of pathogenic organism and its toxicity to aquatic organisms. Under warm climatic conditions it easily looses its contents of dissolved oxygen and become septic, with associated offensive odour. In addition to these, a number of chemicals used in industrial processes which maybe harmful e.g. lead as an antiknock agent in gasoline production, synthetic detergents used in cleaning up, pesticide e.t.c are found in waste water especially industrial wastewater. The environmental implication of dumping untreated waste into seas is highly detrimental to aquatic and human life. Waste water needs to be treated to avoid the underlisted environmental implications.

(i) Land pollution of surface and ground waste bodies.

(ii) Pathogenicity: The spread of communicable diseases.

(iii) Colour: It provides undesirable colour which may affect the colour of the receiving rivers.

(iv) Fish poisoning: Fishes breeding in the receiving stream take in the poisonous chemical associated with untreated waste water e.g. Lead and mercury. These lead to poisoning of man when he eats these fishes.

(v) Plants growth around the outlet stream maybe retarded by the poisonous materials in the wastes water.

(vi) Oil contamination of water bodies in outlet streams: The communities with such polluted water bodies will have problem with the discharging companies for pollution especially oil pollution. A good waste water treatment plant in refinery ensures the recovery of a large quality of crude oil and its products from the waste stream. (Deju Raul, 2001).

1.3 OBJECTIVES

(i) To analyze waste water from the oil industry and compare the result to the standards.

(ii) To know the suitability of this result for agricultural production

1.4 JUSTIFICATION OF THE STUDY.

Wastewater is any water that has been adversely affected in quality by anthroponetic influence. It comprises liquid waste discharged by industry and can encompass a wide range of potential contaminants and concentrations. In the most common usage, it refers to the municipal wastewater that contains a broad spectrum of contaminants resulting from the mixing of wastewaters from difference sources. Sewage is correctly the subset of wastewater that is contaminated with feces or urine, but is often used to mean any wastewater. "Sewage" includes domestic, municipal or industrial liquid waste products disposed of, usually via a pipe or sewer or similar structure. The physical infrastructure, including pipes, pumps, screens, channel etc. used to convey sewage from its origin to the point of eventual treatment or disposal is termed sewerage (wikipedia, 2008).

1.5 LIMITATIONS OF THIS PROJECT WORK

The limitation encountered in the course of this research work was lack of corporation from the local farmers to access the waste water because of damage to the crops.

1.6 SCOPE OF THE STUDY

The scope of this project work is to determine the waste water quality from Kaduna oil refinery and know its suitability for agricultural production.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Characteristics of waste water

The industrial wastewater or effluents are not expected to exceed certain values for examples; some authorities do not permit oil and grease effluent to exceed 20ppm, or (mg/l). For liquids especially fuel and oil effluents, it is describe also to know the electrical conductivity. This is a measure to pick up static charges. This can lead to high energy spark discharges capable of igniting the flammable liquid (e.g. Fuel/air) mixture. To avoid pollution of water and environment relevant authorities in environmental safety generally demand the quality of industrial waste. They insist that liquid effluent discharges especially from petroleum and chemical associated plants shall be monitored at least once a week for the following characteristics (Metcalf and Eddy, 2003).

(1) P^H

(2) Temperature and density

(3) Electrical conductivity

(4) Salinity

(5) Oil grease

(6) Total suspended solid (TSS)

(7) Total dissolved solids (TDS)

(8) Chemical oxygen demand (COD)

(9) Biological oxygen demand (BOD)

(10) Phenols

(11) Leads (PB)

(12) Iron (Fe)

(13) Sodium

(14) Cyanides

(15) Sulphide (as H_2S)

(16) Sulphate (as SO_4)

(17) Ammonia (as NH_4)

(18) Total phosphorus (as PO_4)

(19) Total Nitrogen (as NO_3)

(20) Surfactant

(21) Total Chromium

(22) Discharge rate (gallons or litters per day) etc. (Metcalf and Eddy, 2003).

2.2 PARAMETERS OF REFINERY WASTEWATER AND ITS IMPLICATION ON SOIL

The parameters are generally used for characterizing the various forms of pollutants and largely depend on the nature of the sources of wastewater.

2.2.1 Physical parameters

The Physical characteristics of wastewater include total suspended solid, colour, temperature, odour, turbidity, pH etc. The total suspended solids include floating and suspended solids and dissolved organic substances. The suspended solids clog the soil pores, coat the land surface, and reduce infiltration and aeration. The degree of the problem due to organic content depends on the extent of treatment given to the wastewater prior to its use. The organic material can be beneficial to the soil if managed with aeration and odour problems.

(i) Temperature:

The temperature of refinery waste water in warm climate is slightly lower than air temperature during most of the year. Temperature has effect on microbial activity solubility gases and viscosity.

(ii) **Colours**

The depends on the particular stream and its location, oily water has the colour of the oil, mainly dark if fuel oil is predominant, yellow if diesel oil, clean waste water is clean, fresh sewage is light grey, stale or septic sewage is dark grey or black. The effect of colour on natural water bodies is mainly aesthetic. In places where such water bodies is mainly aesthetic and are uses for washing cloths, no one like to use coloured water for domestic purposes generally.

(iii) **Odour**

Fresh sewage has a somewhat disagreeable earthly, soapy or oil colour. Septic sewage has putrid odours due to hydrogen sulphide involve and other products of decomposition.

(iv) **Turbidity**

This is caused by a wide variety of suspended and colloidal solids. The denser, the wastewater and the more turbid it is. Turbidity can be expressed in the form of total dissolved solids, total suspended solids or conductivity.

(v) **P^H**

The p^H of refinery wastewaters depends on the stream but is generally close to neutral due to treatment in units prior to discharge to the wastewater treatment plant. However, before this pretreatment, stream from the caustic wash unit will be alkaline while that from the hydrofluoric acid alkylation's unit will be acidic. A neutral p^H is attained before discharge to the receptor.(Wesley Eckenfelder,2001).

2.2.2. Chemical parameters.

The chemical characteristics of wastewater include copper, zinc, cadmium and boron. The wastewater receives considerable industrial waste and trace element toxicity such as arsenic, chromium, lead, manganese, mercury. The contents of such chemical contribute to the problem of deficient of the soils. The organic constituent. Include fats; oil and grease which are decomposed slowly by microorganisms. Sewage also contains small fraction of synthetic detergents, phenolic compounds, pesticides and herbicides. These compound depending on their concentration may create problems such as non – biodegradability etc. Measurement of organic contents in refinery wastewater is mainly done by the 5days Biochemical Oxygen Demand (BOD), the amount of oxygen in mg/l that has to be added to a waste water to support the microorganism over a period of 5days. The Chemical Oxygen Demand, (COD) which is the amount of oxygen demanded to chemically oxidize given waste water is also used.

Inorganic pollution parameters include p^H (acidity and alkalinity), chloride, nitrogen, phosphorus, heavy metals (eg) lead, cyanide Nickel, magnesium, variation mercury, phosphate suspended and colloidal solids. Nutrients in wastewater (Nitrogen phosphorus) if discharged in excess cause algae blooms in receiving waters (especially if they are lakes and ponds). There by depleting the oxygen in the water by a process known as eutrophication. (Tchobanogious, 2003)

2.2.3 Biological parameters

The biological characteristics includes bacterial, viruses, algae etc. wastewater can be expected to be teeming with microorganism, some of which may be pathogenic(salmonella, shigella, mycobacterium, and vibrio comma) or disease causing in the soil. Bacterial are the primary decomposer of organic matter (Israelson, 2006).

2.3 HISTORY OF WASTEWATER TREATMENT

In the 19th century, ancient Rome began to understand that they had to reduce the amount of pollutant in the used water they were discharging to the environment. Despite large supplies of fresh water and the natural ability of water to cleanse itself over time, populations had become so concentrated by 1850 that out breaks of life threatening diseases were are traced to bacterial in the polluted water.

Since that time, the practices of wastewater collection and treatments has been developed and perfected, using some of the most technically sound biological, physical, chemical and mechanical techniques available. As a result, public health and water quality are protected better today than ever before. Now, through out the modern world industries, homes, etc. collected their pipes below ground which transport wastewater to the treatment plants before it is released to the environment. At a typical wastewater plants, several million gallons of wastewater flow through each day 50 to 100 gallons for every person using the system. The function of wastewater treatment plants is to speed up the process by which water cleanse (purifies) itself. (Hanson, 2006).

2.4 METHOD OF WASTEWATER TREATMENT

These are the methods involved in wastewater treatments

2.4.1 Preliminary treatment method

The objective of preliminary is the removal of coarse solids and other large materials often found in raw wastewater. Removal of these materials is necessary to enhance the operation and maintenance of subsequent treatment units. Preliminary treatment operating typically includes coarse screening, grit removal and in some cases comminution of large objects. In grit chambers, the velocity of the water through the chamber is maintained sufficiently high, or air is used, so as to prevent a settling of most organic solids. Grit removal is not included as a preliminary treatment step in most small wastewater treatment plants. Comminutors are sometimes adopted to supplement coarse screening and serve to reduce the size of large particles so that they will be removed in the form of sludge in subsequent treatment processes.

2.4.2. Primary treatment method

The objective of primary treatment is the removal of setteable organic and inorganic solid by sedimentation and the removal of materials that will float (scum) by skimming. Approximately 25 to 50 percent of incoming Biological Oxygen Demand ($BODD_5$) , 50 to 70 percent of the total suspended solids (SS), and 65 percent of the oil and grease are removed during primary treatment. In primary treatment, sand, grit, and the larger solids in the wastewater are separated from the liquid. Screens, settling tanks, and skimmering devices are most commonly used for the separation. Primary treatment also removes 45 to 50 percent of the pollutant.

Primary treatment is the minimum level of preapplication treatment required for wastewater irrigation. It may be considered sufficient treatment if the wastewater is used to irrigate crops that are not consumed by humans or to irrigate orchards, vineyards, and some processed food crops. However, to prevent potential nuisance condition in storage or flow-equalizing reservoirs, some of secondary treatment is normally required in these countries, even in the case of non-food crop irrigation.

In large sewage treatment plants primary sludge is most commonly processed biologically by anaerobic digestion process, anaerobic and facultative bacteria metabolize the organic material in sludge thereby reducing the volume requiring ultimate disposal, making the sludge stable (nonputrescible) and improving its dewatering characteristics. Digestion is carried out in covered tanks (anaerobic digesters), typically 7 to 14m deep. The residence time in a digester may vary from a minimum of about 10 days for high-rate digester (well-mixed and heated) to 60 days or more in standard-rate digesters. Gas containing about 60 to 65% methane is produced during digestion and can be recovered as an energy source in small sewage treatment plants, sludge is processed in a variety of ways including: aerobic digestion, storage in sludge lagoons, direct application to sludge drying beds, in-process storage (as in stabilization ponds) and land application.

2.4.3 Secondary treatment method

The objective of secondary treatment is the further treatment of the wastewater from primary treatment to remove the residual organics and suspended solids. In most cases, secondary treatment follows primary treatment and involves the removal of biodegradable dissolved and colloidal organic matter using aerobic biological treatment processes. Aerobic biological treatment is performed in the presence of oxygen by aerobic microorganisms (principally bacterial) that metabolize the organic matter in wastewater. In the secondary treatment wastewater still contains solid materials either floating of the surface, dissolved in the water, or both. Under natural conditions, these substances would provide food for such organisms as fungi, algae, and bacterial that lives in a stream or lake. Secondary treatment is largely a biological process in which air is supplied to stimulate the growth of bacterial and other organisms which consume most of the waste materials. The wastewater is then separated from the organisms and solid, disinfected to kill any remaining harmful bacterial and released to a near by lake, river or stream.

High-rate biological processes are characterized by relatively small reactor volumes and high concentrations of microorganisms compared with low rate processes. Consequently, the growth rate of new organisms is much greater in high-rate systems because of the well controlled environment. The microorganisms must be separated from the treated wastewater by sedimentation to produce clarified secondary effluent. The sedimentation tanks used in secondary treatment, often referred to as secondary clarifiers, operate in the same basic manner as the primary clarifiers. The biological solids removed during secondary sedimentation, called secondary or biological sludge, are normally combined with primary sludge for sludge processing (Wikipedea, 2000).

2.5 WATER QUALITY GUIDELINES FOR MAXIMUM CROP PRODUCTION.

Water is grouped into various quality classes in order to guide the user to the potential advantages as well as problems associated with its use and to achieve optimum crop production. The water quality classifications are only indicative guidelines and their application will have to be adjusted to conditions that prevail in the field. This is so because the conditions of water use in irrigation are very complex and difficult to predict. The suitability of water for irrigation will greatly depend on the climatic conditions, physical and chemical properties of the soil, the salt tolerance of the crop grown and the management practices. Thus, classification of water for irrigation will always be general in nature and applicable under average use conditions.

Many schemes of classification for irrigation water have been proposed. Ayers Wescost, 2007 classified irrigation water into three groups bases on salinity, sodicity, toxicity and miscellaneous hazards. These general water quality classification guidelines help to identify potential crop production problems associated with the use of conventional water sources. The guidelines are equally applicable to evaluate wastewaters for irrigation purposes in terms of their chemical constituents, such as dissolved salts, relative sodium content and toxic ions. Several basic assumptions were used to define the range of values in the guidelines and more detailed information on this is reported by Ayers and Westcott, 2007.

TABLE 1: WASTEWATER QUALITY GUIDELINES FOR IRRIGATION WATER.

Water parameters	Symbol	Unit	Usual range in irrigation water	
			FAO	WHO
Biochemical Oxygen Demand	BOD	Mg/l	0 – 120	_
Acid/base	pH	1 -14	6.0 – 8.5	7.0-8.5
Electrical Conductivity.	EC	0/5/m	0 – 3	< 10000
Total dissolved solid	TDS	mg/l	0 – 829	_
Chemical oxygen demand	COD	mg/l	0 – 120	_
Total Alkalinity	-	mg/l	0 – 322	0- 100
Total Hardness	-	mg/l	0 – 225	_
Total Suspended solid	TSS	mg/l	0 – 45	10-70
Copper	Cu	mg/l	0.5	0-2.0
Iron	Fe	mg/l	2.0	0.05-0.3
Manganese	Mn	mg/l	0.2	0-0.5
Lead	Pb	mg/l	0.05	0-0.01

Source (FAO and WHO, 2001).

TABLE 2 NORMAL CONTENT INTERVALS OF HEAVY METALS IN SOIL.

Chemical element	Normal content interval mg/l
Mn	0 – 1.0
Cr	0 – 2
Cu	1 – 20
Ni	0 – 5
Pb	0.1 – 20
Zn	0 – 2.0

Source (www.pcd.go, 2004)

2.6 CONSEQUENCES OF WASTEWATER IN AGRICULTURAL PRODUCTION.

The chemical quality of water determines its suitability for agricultural use. The chemical constituents of wastewater are the major source of water contamination which leads to water quality degradation and salinity problems.

(a) **Salinity:** This is the presence of soluble salt in the root zone of the crop. For instance in irrigation purpose, some chemicals will be injected into the irrigation water for application in the field. This irrigation water contains dissolved salt, which remain in the soil after water use by evapotranspiration. This salt must be removed to maintain crop production and natural or artificial drainage systems are needed to remove associated salts from the plant root zone. Salt affected soils may be classified as saline, sodic or saline – sodic soils.

(i) Saline soil contains sufficient soluble salt to interfere with the growth of most plants. Saline soils it will be recognized by the presence of white crusts on the soil, by spothy stands, and by stunded and irregular plant growth. The main effect of salinity is to reduce the availability of water to the plant. In case of extremely high salinity, there may be curling and yellowing of the leaves, firing in the margins of the leaves or actual death of the plant. (Ayers and Westcott, 2007)

(ii) Sodic soil contains low soluble salts, but contain sufficient adsorbed sodium. When excess sodium is absorbed on the surfaces of the fine soil particles it is not leached readily unit is being displaces by other cation, such as calcium or magnesium.

The proportion of exchangeable sodium increased, soil tends to become dispersed, less permeable to water and of poorer tilth. High sodium soils are usually plastic and sticky when wet, and are prone to form clods, and crusts on drying. These condition results in reduced plant growth, poor germination, poor root aeration. (Merriam and keller, 2003).

(iii) Saline – sodic soils contain sufficient quantities of both soluble salt and adsorbed sodium. When excess amount of soluble salt and sodium is applied by irrigation it result to the reduction of crop yield. (Merriam and Keller 2003).

(b)Toxicity: A toxicity problem occurs when certain constituents in the wastewater are taken up by the crop and accumulate in amounts that result in reduced yield. Thhisis usually related to one or more specific ions in the water such as, boron, chloride and sodium.

(C) Miscellaneous: This is due to excess of nitrogen in the water. The excess of nitrogen result in excessive vegetative growth, lodging and delayed crop maturity (Michael, 2000).

2.7 EFFECT OF SEWAGE SLUDGE ADDITION ON HEAVY METAL CONCENTRATIONS IN AGRICULTURAL SOILS.

Land application of sewage sludge has been a worldwide agricultural practice for many years. Although sewage sludge provides essential plant nutrients and organic matter for plant growth, its continual use over extended periods can result in accumulation of heavy metals to levels detrimental to the environment. Such enhanced soil metal contents may result in reduced plant growth (alongside other symptoms of phytotoxicity); metals can enter the food chain via human consumption, and are therefore of interest in regard to their potential impact on human health. Recently, this has been identified as a prime problem in the agricultural lands of the areas surrounding New Delhi, the capital city of India. For the reported study, soil samples were collected from ten spatially variable locations from an agricultural field in New Delhi, which was historically (exact duration unknown) amended with domestic sewage sludge of unknown chemical composition. The practice ended in the later part of the last century. Uncontaminated control soils were collected from one location in the vicinity (a residential garden soil) for comparison purposes. The primary focus of the study was to evaluate the effect of long-term application of sewage sludge on the geochemical fate (and hence, phytoavailability) of heavy metals in agricultural soils. The sludge-impacted soil samples are currently being analyzed for total concentrations of heavy metals typical to sewage sludge, namely Chromium, Copper, Cadmium, Nickel, Manganese, Zinc, Leed, Iron as well as for their plant available fractions (soluble and exchangeable forms) in comparison with the control soil. Because soil properties play an important role in the retention/release characteristics of heavy metals, the soil samples are also being characterized for selected physico-chemical properties, such as texture, pH, salinity, cation exchange capacity, organic matter content, and total and extractable concentrations of Calciun, Magnesium, Iron, Aluminum and Phosphorus. The soil properties will be correlated with total and available heavy metal concentrations to quantify their relative effects on metal uptake potential by plants.

2.8 INORGANIC MINERALS AND CHEMICAL COMPOUNDS.

These are measured in parts per million (ppm) by weight or mg/l and can kill or harm fish and other aquatic life and can interfere with the suitability of water for drinking or industrial use. The example is mercury, anaerobic bacteria in button mud can convert inorganic mercury into methyl mercury ($CH3Hg$), which can be concentrated in living organisms and lead to mercury poisoning. Other inorganic minerals include bromine iodine, magnesium and sulphour. The first three which is bromine, iodine, magnesium could be seen in brine discharged along with crude oil to the surface during petroleum drilling.

2.8. 1. Sediments

Sediments are soil and mineral particles washed in the land by storms and flood waters, from crop lands, unprotected forest soils, ove zed pastures, strip mines, roads and bulldozed urban areas. Sediments fill stream ch and reservoir, erode power turbines and pumping equipment, reduced the amou light available to green aquatic plants, plug water fitters and blanket fish nets, spawn and food suppliers thus reducing the fish and shell fish population.

2.8.2 Radioactive substances

Harmful radiation may result in water environment from the wastes of uranium and thorium mining and refining from nuclear power plants and from industrial, medical and scientific utilization of radioactive materials.

2.9 TYPES OF WASTE.

The effective waste management strategies can be the amount of waste generated and their sources, but also the materials in each waste stream, their properties, potential toxicity and hazards to human health and the environment. The lack or reliable time series of waste arising and damage in waste stream is a serious impediment to settling priorities in waste management in many developed as well as developing countries. Wastes are produced by all society activities and include;

(i) Household and consumer wastes

(ii) Agricultural wastes

(iii) Industrial waste

(iv) Demolition and construction wastes.

(v) Extractive wastes

(vi) Sewage sludge e.t.c. (Metcalf and Eddy, 1979).

CHAPTER THREE

3.1. LOCATION OF PROJECT AREA

The Kaduna Refinery and petrochemical company is located at southern part of Kaduna metropolis which lies between longitude 7° 251 and 8° 251 east, and latitude 4° 321 and 5° 321 north.

3.2. HYDROLOGY OF STUDY AREA.

The Kaduna refinery and petrochemical company waste water is the main tributary to the Rome river. The Rome River flows through mainly settlement before entering into river Kaduna. The Kaduna in which the study is made at the refinery has a relative humidity range of 75-85%.

3.3 SAMPLE COLLECTION.

The samples were collected in three stations in the study area. From each station two litres of waste water was collected in clean plastic bottles. The sarles were taking into the laboratory for analysis that same day.

3.4. METHODS OF ANALYSIS.

3.4.1 WASTE WATER ANALYSIS.

The waste water analysis was carried out in water res(and aquaculture, fishery Technology Laboratory (WAFT) and soil science laborat(ectively. Both in Bosso Campus Federal University of Technology Minna, Niger he water aspect was done at soil science laboratory.

3.4.2 SOIL ANALYSIS

Samples were collected from the top-soils (0-20 cm) of agric s. The total content of heavy metals was measured using atomic absorption s the flame atomization method. Soil digestion was carried out by using a n centrated

$HClO_4$ and HNO_3 at a 2:1 ratio; then, by dissolving the precipitate in HCl 0.5 n, a solution was obtained in which spectrometric measurements were made.

3.4.1.1 DETERMINATION OF TEMPERATURE.

This is determined by using thermometer. The probe was immersed in distilled water to rinse. The probe also immersed in beaker containing the sample and allowed to read. The reading was recorded in degrees Celsius (c).

3.4.1.2 DETERMINATION OF BOD_5.

This is determined by mixing 10ml of sample and 300ml of distilled water properly mixed and transferred into BOD bottles. The dissolved oxygen of the water sample was determined on the first day and same sample was incubated at room temperature for 5days in the dark before titration. On the 5^{th} day, the sample was removed and brown precipitate was formed. The precipitate was dissolved by adding cone. H_2SO_4. Then, I add manganous sulphate and potassium sulphate and titrate with sodium thiosulphate. The reading was recorded in mg/l. the method used is Winkler azide method.

BOD5mg/l = dissolved oxygen on day1 – dissolved oxygen day**5.**

3.4.1.3 DETERMINATION OF p^H

The pH of the water sample was determined with a digital pH meter at room temperature. The meter was standardized with buffer 4 and 7 respectively before taking the reading. The probe of the meter was rinsed thoroughly with distilled water before inserting it into 50ml conical flask which the water sample was pounced

3.4.1.4 DETERMINATION OF ELECTRICAL CONDUCTIVITY.

This is determined by using Jen way 4010 conductivity meter. 50ml of the sample was measured and transferred into 250ml conical flask. The probe of the meter was rinsed thoroughly before inserting it into the conical flask that contained the sample and the conductivity of the sample was determined. He reading is expressed in Ns/cm.

3.4.1.5 DETERMINATION OF TOTAL DISSOLVED SOLIDS (TDS).

This is determined by heating 250ml beaker in an electric oven at 120c for I hour. 50ml of sample was measured and filter through using a filter paper. The filtrate was transferred to the pre – weighed evaporating beaker and evaporated to dryness on a hot plate and transferred to electric oven for complete drynen and allow to cool then weighed.

3.4.1.6 DETERMINATION OF CHEMICAL OXYGEN DEMAND (COD).

50ml of sample of waste water was transferred into a 250ml conical flask and I added 10ml of KMno4 solution and 10ml of H_2SO_4 solution. Then I mixed gently and placed it on a thermostat hot plate for gradual heating at 100.c and heat for 2 hours until the sample remains 10ml. when the sample remains 10ml I removed it from the thermostat hotplate and allow to cool. After that, I added 10ml of potassium iodide (KI) and titrate with sodium thiosulphate, using starch as an indicator until it charges colourless, then I recorded the result. The blank sample was processed and titrated in the same way.

3.4.1.7 DETERMINATION OF ALKALINITY.

50ml of sample of waste water was measured and transferred into a 250ml conical flask. Then I added 4 drops of methyl orange indicator and titrated with 0.02N of H_2SO_4 until it changes pink, then I recorded the result.

3.4.1.8 DETERMINATION OF TOTAL HARDNESS.

50ml of sample of waste water was measured and transferred into a 25oml conical flask and I added 1ml of NH_3 buffer solution to elevate the p^H and tiny amount of dry – erichrome black T indicator. After added 1 ml of NH_3 buffer solution and tiny amount of dry – erichrome black T indication the solution starts out wine red, when the indicator end point was reached the red turns to blue. Then I titrate the sample slowly with 0.01m EDTA. (Ethylene diamine Tetra acetic Acid) until the last reddish tinge disappears from the solution, then I added five drops of EDTA to allow the end point reaction to go completion. Then I record the result obtained.

3.4.1.9 DETERMINATION OF TOTAL SUSPENDED SOLIDS (TSS).

The weight of filter paper was measured before filtration and I accurately measure 50ml of sample and transferred into the filter paper placed on the funnel for filtration. Then, after the filtration I washed the remaining solids from the 250 conical flasks with distilled water. The filter paper was removed and dried in an electric oven at $105^{°c}$ for 30mins which was allows to cool and reweighed. The amount of suspended solids is determined from the increase in weight of the filter paper.

3.5 REAGENTS AND MATERIALS.

The reagents and materials for the laboratory analysis are:

- Three 2 litres plastic bottles.
- BOD bottles
- 500ml volumetric flask.
- Pipette

- 250ml concal flask
- Funnels
- Thermometer
- pH meter (Jen way model).
- Jen way 4010 conductivity meter.
- Thermostatic hot plat.
- 250ml beaker
- Electric oven
- Potassium permanganate solution (KMno4).
- Tetraoxosulphate vi acid solution (Conc. H_2SO_4)
- Potassium Iodide (KI)
- Sodium Thiosulphate
- Starch solution
- Manganous sulphate
- Potassium Sulphate.
- Methyl orange indicator.
- Ammonia buffer (NH_3 buffer)
- Dry – erichrome black T indicator.
- Ethylene diamine Tetra Acetic acid (EDTA).
- Distilled water.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 Presentation of results

TABLE 3: RESULT OF LABORATORY ANALYSIS.

S/N	PARAMETERS	STATION1	STATION 2	STATION 3
1	Temperature ◦C	29.6	29.6	29.6
2	BOD_5(mg/l)	24	36	88
3	p^H	6.30	6.54	7.91
4	Electrical conductivity (ds/m)	0.425	0.375	0.285
5	Total dissolved solid (mg/l)	0.6	0.6	1.0
6	COD (mg/l)	40	44	60
7	Total Alkalinity (mg/l)	41	40	40
8	Total Hardness (mg/l)	64	56	48
9	Total suspended solid (mg/l)	0.2	0.4	0.2
10	Copper (mg/l)	0.09	0.07	0.10
11	Iron (mg/l)	0.01	0.01	0.0
12	Manganese (mg/l)	0.18	0.12	0.14

13	Lead (mg/l)	0.79	0.72	0.60

TABLE 4: RESULT OF LABORATORY ANALYSIS FOR SOIL

S/NO	PARAMENTERS	SYMBOL	VALUE
1.	Zinc	Zn	0.02
2.	Nickel	Ni	0.08
3.	Chromium	Cr	0.005
4.	Manganese	Mn	0.03
5.	Copper	Cu	0.006
6.	Lead	Pb	0.001

4.2 DISCUSSION OF RESULTS.

4.2.1 TEMPERATURE

Temperature of irrigation water can have a significant effect on plant growth. When the temperature is lower or higher than that of the soil, it can lead to plant shock. It is therefore advisable to irrigate during the period of less heat of the day.

4.2.2 BIOLOGICAL OXYGEN DEMAND (BOD_5).

The Biological Oxygen Demand is the oxygen required for the biological decomposition of the organic matter in waste water. It is determined by measuring the amount of oxygen used by decay microorganisms in a sample of the wastewater over a specific period of time, usually five days. The Biological Oxygen Demand is indicative of the impact that the wastewater can be expected to make on the oxygen content of the stream receiving the waste. The usual range for Biochemical Oxygen Demand by FAO is between 0- 120mg/l, but the readings show that the level of BODs is normal between the ranges which are: 24.0, 36.0, 88.0 respectively (Encyclopedia Americana, 2001)

4.2.3 P^H

The P^H is a variable that regulates all biological function. Sometimes it has an inhibitory effect on process rates. It is the degree of acidity or alkalinity to soil or irrigation water. Recommended value ranges from 6.5 – 8.5 and 7.0-8.5 by FAO and WHO respectively, the P^H scale is from 0 – 14, seven is the neutral point while from seven to one shows increase in acidity, similarly from seven to fourteen indicates increase in alkalinity. The values obtained from the three stations are 6.30, 6.54 and 7.91 respectively. These values are within the normal range. (John H et al 2006).

4.2.4 ELECTRICAL CONDUCTIVITY:

Electrical conductivity is the measure of salinity. It is the ability of irrigation water to conduct electricity. This is as a result of total dissolved solids in the water. These dissolved solids are mostly positively charged ions as well as negatively charged ions in irrigation. Excessive salinity can affect plants by specific toxicity of a particular ion (such as sodium), higher osmotic pressure around the plants roots prevents an efficient water absorption by the plant. The recommended value by FAO and WHO ranges from 0-3mg/l and < 10000mg/l respectively. The values obtained from the three stations are 0.425, 0.375 and 0.285

Respectively. These values fall between the normal ranges. (John L.H et al 2006).

4.2.5 TOTAL DISSOLVED SOLIDS:

The presence of solids in suspension usually made from clay or from other material derived from drainage waters, generally does not cause significant damage to crops. Clay and silt deposits affect irrigation canals in every part of world. The recommended value from FAO and WHO ranges 0-45 and 10-70 respectively These values obtained from the three station are 0.2, 0.4 respectively and they are within the range.

(Glenn Schwab, 2001)

4.2.6 Copper.

A common form of metal pollution is the direct discharge of untreated wastewater from industrial sources into receiving waters. When large amount of copper is discharged, ammonium sulphate in the wastewater caused nitrate to accumulate in the river, resulting in progressive acidification. The recommended value from FAO and WHO ranges from 0-0.5 and 0-2.0 respectively. The values obtained from the three stations are 0.09, 0.07 and 0.10 respectively and they are with the range. (John Smol, 2002)

4.2.7 Iron

Iron is an essential micronutrient that helps in the formation of chlorophyll. It activates a number of important respiratory in plants. It is absorb principally as Fe^{3+} ions and also as Fe^{2+} ions. The deficiency results in severe chlorosis of the leaves, especially the young leaves. The recommended value from FAO and WHO ranges from 0-2.0 and 0.05-0.3 respectively. The values from the three stations are 0.01, 0.01 and 0.0 respective. They fall within the normal range. (Michael and Ojha, 2005)

4.2.8 Chromium

Chromium is heavy metal that is not generally recognized as an essential growth element. The recommended value by pollution control department, ministry of national resources and environment is 0 – 2mg/l, the value I obtained is 0.005mg/l, this is within the range of the standard.

4.2.9 Manganese

Manganese is toxic to number of crops at a few tenth. The recommended values is 0 – 1.0mg/l and the value I obtained is 0.03mg/l, this is within the range of the standard.

4.2.10 Nickel

This is toxic to a number of plants at very low tent. The recommended value is 0 – 5mg/l and the value I obtain is 0.02, this is within the range of standard.

CHAPTER FIVE

5.0 CONCLUSION ND RECOMMENDATION

5.1 CONCLUSION

Conclusively, the waste water sample from the three stations that is taken are good for agricultural purposes terms of quality and quantity. Although, it was observed that the parameters are within the specified range or given standard according to food and agricultural organization (FAO), and World Health Organization (WHO), that it may not cause severe damage to the crops.

5.2 RECOMMENDATION

It was observed that the heavy metals such as chromium, copper, zinc, manganese, nickel with values of 0.005, 0.006, 0.02, 0.03 and 0.08 mg/l respectively are within the standards of W.H.O (2001), FAO (2001), NAFDAC (2004) and SON (2001) showing a high level of self purification before arriving at the points where the samples were collected. It is therefore recommended that the area is good for agricultural purpose.

REFERENCES

Ayers, R.S and D.W Westcott (2007). Water quality for Agriculture irrigation and Drainage. Paper No. 29, Rev 1. FAO, Rome, Italy. John Wiley Inc. & Sons pp 15-25

Deju Raul .A. (2001). The environment and its resources. Urban and breach, science publishers. Pp. 194 – 201.

Encyclopedia American, international, (2001). Edition completed in thirty volumes, volume 28. Grolier incorporated 425 pp.

Glenn O. Schwab (2003) Soil and water conservation engineering. Pp. 374 – 393. professor emeritus of Agric. Engineering Ohio state university Columbus, Ohio. John Willey & sons, Inc.

http://en.wikipedia.org/wiki/waste water 11-16-2009.

http://www.fao.org/docrep/to551e/to551eo5.htm11-17-2009.

Israelson, O.W and Hanson, V.E (2006) irrigation principles and practices 3rd edition. John Wiley and sons, New York. Pp 207-2011

John. L.H (2006). Soil fertility and fertilizer. Practice hall ltd. New Delhi. Pp 83-97.

John Smol. P, (2002). Pollution of lakes and rivers. Department of biology, Queen's University, Kingston, Ontario, Canada. Oxford University press inc. New York pp 113-114.

Merriam, J.L and J. Keller (2003). Farm irrigation system evaluation: a guide for management. Agric and irrigation engr. Dept, Utah State University, Logan, UT. Pp 180.

Michael .A.M (2000) irrigation theory and practice. Vikas publish, New Delhi. pp 710.

Michael A.M and Ojha T.P. (2005) principles of agricultural engineering. Jain brothers publishers, New Delhi. Pp 123.

Shwab, G.O (2001) soil and water conservation engineering, 4^{th} edition. John Wiley and sons Inc. New York. Pp 217-230.

Tchobanogious.G (2003). Waste water engineering. 4^{th} edition McGraw-Hill, Inc. 205pp.

APPENDIX

Total dissolved solids (TDS) = $\frac{1000(MP - MB)}{50}$

Mp = Weight of dried beaker + sample

Mb = Weight of dried beaker.

Station 1: TDS = $\frac{1000(86.45 - 86.42}{50} = 0.6mg / l$

Station 2: TDS = $\frac{1000(73.68 - 73.65)}{50} = 0.6mg / l$

Station 3: TDS = $\frac{1000(76.21 - 76.16)}{50} = 1.0mg / l$

Chemical Oxygen Demand (COD) = $\frac{(A - B)xNx1600}{Volumeofsample}$

A = control

B = Titrated value

Station 1: COD = $\frac{3.2 - 2.2x0.025x16000}{10} = 40mg / l$

Station 2: COD = $\frac{3.2 - 2.1x0.025x16000}{10} = 44mg / l$

Station 3: COD = $\frac{3.2 - 1.70x0.025x16000}{10} = 60mg / l$

Total Alkalinity = $\frac{AxNx50,000}{volumofsample}$

A = Titrate of value

N = 0.02N of tetraoxosulphate Vi solution

Station 1: Total Alkalinity = $\frac{2.05x0.02x50,000}{50} = 41mg/l$

Station 2: $\frac{2.0x0.02x50,000}{50} = 40mg/l$

Station 3: $\frac{2.0x0.02x50,000}{50} = 40mg/l$

Total Hardness = $\frac{AxBx100}{volumeofsample}x1000$

A = Titrated value

B = 0.01m of Ethylene diamine tetra acetic acid (EDTA).

Station 1: Total hardness = $\frac{3.2x0.01x100}{50}x1000 = 64mg/l$

Station 2: Total hardness = $\frac{2.8x0.01x100}{50}x1000 = 56mg/l$

Station 3: Total hardness = $\frac{2.4x0.01x100}{50}x1000 = 48mg/l$