# MODEL DEVELOPMENT FOR LIQUID EFFLUENT DISCHARGE OF SOME PARAMETERS INTO THE RIVER, USING KADUNA REFINERY AND PETROCHEMICAL COMPANY (KRPC) AS CASE STUDY.

BY

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A PROJECT SUBMITTED TO THE DEPARTMENT OF CHEMICAL ENGINEERING, FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA.

IN PARTIAL FULFILMENT OF THE REQUIREMENT FOR THE AWARD OF B.ENG (CHEMICAL).

**0CTOBER, 2004.** 

#### **DECLARATION**

1, Mustapha, Amina Tani (98/7081EH), declare that this project is my original work and
has never been submitted else where before, to the best of my Knowledge.

Signature

Date

#### **CERTIFICATION**

This is to certify that this project was supervised, moderated and approved by the following under-listed people, on-behalf of the Chemical Engineering Department, School of Engineering and Engineering Technology, Federal University of Technology, Minna.

A LIFE	·) ·) · ((· · · ·
Engr. M.A Olutoye	Date
Project Supervisor	
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Head of Department	
External Supervisor	Data

#### **DEDICATION**

This is dedicated to the Almighty Allah (S.W.T) who has seen me through out my programme, my dear Parents for their total support and to my beloved Husband and Daughter, for their love, understanding, caring and prayers in all my endeavours.

#### **ACKNOWLEDGEMENT**

Praise be to Almighty Allah, my Creator who has given me life and good health to complete my course in this University and for Him seeing me through the successful completion of this project.

My profound gratitude goes to my Supervisor, Engr. Olutoye whose advice and encouragement helped in no small amount for this work to come to a reality.

I am also thankful to my Lecturers: Dr. Aberuagba, Dr. K. Onifade, Dr. Odigure, Dr. Edoga, Dr. Duncan, Engr. (Mrs.) Eterigho, Engr. S.A Abdulkareem, Engr. Abdulfatai, Engr. Agbajelola, Engr. Akpan, Engr. Kovo, Engr. Alhassan and other staff of Chemical Engineering Department.

I am highly indebted to my Parents Alhaji Muhammad Mustapha and Hajiya

Aishat Mustapha for their love financial and moral support. My appreciation goes to the entire Mustapha family for their contributions to my education.

My heartfelt thanks go to my Husband (Alhaji Y. Umar) and my little princess (Hauwa Kulu) for their love, care understanding and support.

Special thanks go to my friends too numerous to mention, for their understanding and support throughout my stay in this Campus.

Once again, I am grateful to Almighty Allah (S.W.T), without who nothing is possible and who has spared my life to this time. May His blessings be upon the seal of the Prophets (Amin).

#### **ABSTRACT**

This project was an attempt to develop a mathematical model for some parameters contained in Liquid effluent discharged into the river using Kaduna Refinery and Petrochemical Company (KRPC) as case study and Romi river as a specific case study.

Experimental data were collected from KRPC over a period of three months and the analysis of the data carried out to know the factors that affect the pH of the liquid effluent s most. Model equations were developed for the pH based on the analysis of the data results obtained. These parameters include Temperature, Biochemical Oxygen demand (BOD), Turbidity, Total dissolved Solids, Dissolved Oxygen among others. The model was obtained using MathCAD and Excel Programming Softwares.

The results obtained, showed a slight deviation from the experimental pH. A typical model expression for May 2004 is given below.

 $pH\ model:=0.18.T-0.00393.U+0.006797.D+0.008037.O+0.043.B-0.025.C\\ +2.578.D-0.159.P-0.033.S$ 

Generally it was observed that there is a slight increase in the modeled pH as against the experimental value. This suggests that some experimental parameters were not determined, due to faulty equipments and lamp failure.

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#### **CHAPTER ONE**

#### 1.0 INTRODUCTION

#### 1.1 BACKGROUND OF STUDY

The need for treating Industrial waste water before being discharged into any river body cannot be over emphasized. Many processing Companies utilize large volume (quantity) of water in this Course of production with little or no treatment given to this waste water (by product) thereby posing danger to both plants and animals. Chemical Engineers in their capacities are concerned with the maintenance of the guidelines stipulated as the threshold limit values of these water contaminants.

During processing of petroleum in KRPC, liquid effluent is the major by product with minimal solid wastes and gaseous effluent. Hence for this project to be within a reasonable scope, attention is focused only on the impact of liquid effluent to the receiving water body.

Indiscriminate discharge of wastes; both Domestic and Industrial effluent have adverse effects on the quantity of water resources. Water as an important input of production has to be preserved in quality. Effective implementation of the environmental guidelines and standards for pollution control by FEPA gives a better protection of the water body(river) from pollution.

It is the duty of Individuals, Societies, National and International bodies to protect water/river against an overload by sewage so as to preserve it for various utilization by man.

In order to achieve this, all Manufacturing and Processing Industries are forced to control the amount of disposed water and the concentration of harmful impurities as well as monitoring carefully, the residual influence on the receiving water body (FEPA).

One of the methods of achieving this, is by modeling of analytical data given for the liquid effluent so as to take measures and control of the impurities present in the waste water for subsequent use. Modeling can be described as the determination of a quantitative picture of an important system Characteristic. It could be inform of collected data, analytical studies or Computer simulation of the actual system.

The interest is in formulating Mathematical Models that yield reasonable accurate descriptions or prediction about a given system, while minimizing Computational and Programming time. Modeling and Simulation can be carried out with the aid of some softwares like Excel MathCAD e.t.c (Bryan William Scotney).

#### 1.2 AIMS OF THE PROJECT.

The aim of this Research work is to develop a Mathematical Model for liquid effluent discharge of some parameter into (water) rive in an Industrial area, Case study of KRPC. This can be achieved through the following processes:

- i. Collection of data.
- ii. Analyzing the data.
- iii. Modeling.

### 1.3 SCOPE.

In order to ensure that adequate Information of the various parameters present in liquid effluent (waste water) from KRPC were obtained for this work, data used were collected at various seasons and stages.

#### **CHAPTER TWO**

#### 2.0 LITERATURE REVIEW.

#### 2.1 MATHEMATICAL MODELING.

Mathematical modeling is an explicit technique for representing real world phenomena in terms of Mathematical equations which gives a good understanding of the phenomena and can be used to predict likely occurrences. The model equations and number of variables must be equal i.e. "degree of freedom" of the system must be zero. (William 1990). Model is a simplified representation of a system intended to enhance our ability to understand, explain, change, preserve, predict and possibly control the behaviour of a system (Naelamkavil 1987), James (1973), defined a model as a representation of a system in a form suitable for demonstrating the way the system behaves.

Mathematical Modeling has wide areas of applications in Chemical Engineering, from Research and Development, to plant operations and even in Business and Economic studies. (Luyben, 1995). In developing a Mathematical Model, the necessary parameters need to be identified, in order to obtain a very good representation or approximation of the actual process.

#### 2.2 CLASSIFICATION OF THE MATHEMATICAL MODELS.

Mathematical Model can be grouped into two classes, namely; DYNAMIC and STEADY STATE MODELS.

1.DYNAMIC STATE MODELS are time dependent models.

2. STEADY STATE MODELS shows the interactive behaviours of the system at steady state.

Dynamic models are further classified into continuous time and discrete time models. (Luyben, 1995).

Another classification of the Mathematical Model is the STOCHASTIC(Probabilistic) and DETERMINISTIC models. Stochastic models have at least one random variable in their description Model other than these are called Deterministic. (Luyben, 1995).

#### 2.3 PRINCIPLES OF MODEL FORMATION.

In forming mathematical Models the following Principles ought to be applied.

#### 2.4 BASIC.

The basis is the fundamental, physical and chemical laws like laws of energy, mass conservation and momentum. In studying the dynamics, the time derivatives are also included.

#### 2.5 ASSUMPTIONS.

In making assumptions, care must be taken as these serve as limitation beyond which the Model would not hold. It is necessary to make simple but reasonable assumption while modeling. A simple Model needs many assumptions and yields an approximate result quickly, while a complex model of the same system needs just few assumptions to give an accurate answer by the use of more advanced Mathematical techniques.

#### 2.6 MATHEMATICAL CONSISTENCY OF A MODEL.

The number of variables and equations describing any system or process must not be under-specified or over-specified. The o-called degree of freedom" of the system must be zero, i.e. the number of variables must equal the number of equations in order to obtain a solution. The unit of term used in the equations must also be in consistency.

#### 2.7 SOLUTION OF THE MODEL EQUATION.

When the model has been developed, certain approximations and boundary conditions ought to be taken, outside which the required solution cannot be obtained. The equations should be those which could be solved by the available techniques without much difficulties.

#### 2.8 VERIFICATION.

This is an important aspect of Mathematical Modeling, aimed at proving that the model actually describes the real world situation. One way of achieving this aim, is by comparing the experimental result to the Computer results.

#### 2.9 SIMULATION.

Simulation of a system is designed as the operation of a model, which is a representation of the system, the model being amenable to manipulation which would be impossible, too expensive or impracticable to perform on the system it portrays (Martin Shubik).

A Computer Simulation is used to predict the effect of changing conditions and capacity of mass energy balance and to optimize operation easily and quickly. It provides in-depth Knowledge about complete system behaviour, improve and facilitate cost evaluation and planning of operations.

#### 2.10 SIMULATION PROCEDURE.

The logical steps of Simulation are listed below:

- 1. Data Collection.
- 2. Analysis of the problem.
- 3. Simulation and Model specification.
- 4. Model Programming.
- 5. Model Verifications.
- 6. Simulation Experiments.
- 7. Evaluation and Interpretation of Simulation results.
- 8. Report generation.

In Summary, the aims of Modeling and Simulation are itemized below:

- 1. To estimate the process variable which are not directly measurable.
- 2. To predict system behaviour in different levels, where any level of predictive ability represents a benefit.
- 3. To improve understanding of some mechanisms in the studied process.
- 4. To optimize system behaviour and efficient fault diagnoses.

Modeling and Simulation as a means of control measure becomes necessary in this project as a result of constant monitoring of environment required in KRPC area and its environs, to evaluate the extent of pollution caused by waste water. Modeling could eliminate time and material wastage in carrying out experimental work aimed at finding the impact of waste water on the river body.

#### 2.11 LIQUID EFFLUENT CHARACTERIZATION.

Liquid effluent is obtained as a result of various processing and stages of production of liquid effluent (waste water) becomes contaminated with either solid, liquid or gaseous substances or Compounds which in turn causes some changes in the Physical and Chemical properties in water.

The Physical properties (characteristics) are used in qualifying the Physical appearance of the waste water, examples of these includes; Tastes and Odour, Temperature, Turbidity, Suspended particles, Colour, e.t.c. A brief explanation of some of these properties are given below.

- Taste and Odour which may be due to dissolved impurities, examples like
   Phenol and Chlorophenols.
- Temperature: Temperature have effects on some other properties like in speeding up the rate of Chemical reaction.
- Turbidity could be due to Clay and Silt particles, discharge of Industrial wastes which gives a cloudy appearance and may be harmful.
- Colour: This is the effect of the Industrial waste particles which may be present in liquid effluent. The colour usually depends on the nature of the materials in it.

The Chemical properties of liquid effluent are of two categories; The Organic and Inorganic matters present in it. The test used to determine the Organic contents are biochemical Oxygen demand (BOD), dissolved Oxygen (DO), Chemical Oxygen demand (COD), Phenols, Oil concentration, e.t.c.

Determination of Inorganic contents of liquid effluent carried out by the following tests; pH, alkalinity, acidity, sulphates, heavy metals (such as Lead, Mercury, Silver, e.t.c.). Some important Chemical Characteristics are described below.

pH: It measures the concentration of hydrogen ion present in it. The intensity of acidity or alkalinity of Industrial waste water sample is measured on pH scale.

Dissolved Oxygen(DO): Oxygen is an important element in water quality control, as it is needed by both plants and animals for their well-being, since most of the liquid effluents are discharged into the river, the level of dissolved Oxygen ought to be known as it has impact on the aquatic lives.

# 2.12 \*TABLE. SOME EXAMPLES OF "WHO" GUIDELINES FOR DRINKING WATER QUANTITY.

CHARACTERISTIC	ACTION LEVEL
Arsenic	0.05mg/l
Cadmium	0.005mg/l
Chromium	0.05mg/l
Cyanide	0.1mg/l
Fluoride	1.5mg/l
Lead	0.05mg/l
Mercury	0.001mg/l
Nickel	0.1mg/l
Nitrate and Nitrite	10mg/l
Selenium	0.01mg/l

Chloride	250mg/l
Sulphate	400mg/l
Hardness as in CaCo <sub>3</sub>	500mg/l
Total dissolved Solids	1000mg/l
Aluminum	0.2mg/l
Chlorophenols	0.1µg/l
Chloroform	30µg/l
Monochlorobenzene	3.0µg/l
1,4-dichlorobenzene	0.1µg/l
pH	6.5 to 8.5µg/l

<sup>\*</sup>Guidelines for drinking Water Quality, WHO, Geneva, 1984

#### 2.13 EFFECTS OF LIQUID EFFLUENT ON MAN AND ENVIRONMENT

Liquid effluent of large quantities (volume) are being discharged from Industrial Companies into the river annually which have effect on both man and environment. Waste water from processing Industries contain a lot of hazardous particles or substances which could be in low or higher concentration, depending on the nature of such industries. For instance, Petroleum Industries like KRPC will have liquid

effluent with high concentration of Organic Compounds and certain percentage of non-organic compounds present in it. These compounds adversely affect the health of man, animals and cause damages to plant and materials as well as aquatic life.

The global effects of water pollution on man and his environment due to increased levels of phenols, Chlorophenols, benzene, heavy metals (such as Silver, Mercury, Lead) as well as non-metals (like Arsenic) in poisoning and severe toxicity to both living organisms and non-living organisms (material damages) cannot be over-emphasized. The main concern in water supply is the presence of low levels of contaminants which may produce observable health effects after long exposure, perhaps after many years, some potentially harmful substances appear to have a threshold effect in the sense that, provided the concentration remains below some critical level, no harm is caused. Other contaminants appear not to have a threshold level, so that any intake is potentially harmful and substances which cause Cancer (Carcinogens) often follow this pattern. Contaminants, particularly potential Carcinogens such as polyaromatic hydrocarbons (PAH) trihalomethanes (THM) and organochlorine as well as organophosphorus compounds, it is advisable to ensure that their concentrations in drinking water are kept as low as possible.

Liquid effluent also contains significant amount of Nitrogen in form of nitrate. Its presence in drinking water has not shown any harmful effect on adults and children but it can be dangerous for bottle fed babies up to age of six months. At this stage, babies lack the normal bacterial flora in their intestines which deal with the nitrite produced by the reduction of nitrate in the stomach. The nitrite when absorbed into

the blood, prevents Oxygen transport and causes Methaemoglobinemia or "blue-baby disease". (T.H.Y TEBBUTT).

In Summary, pollution causes an economic loss due to the damages and destruction of resources required by man for the normal living standard of life. In other words, a polluted environment posses risks to health of all living things, economic well being of man, as well as development.

#### CHAPTER THREE

#### 3.0 EXPERIMENTAL DATA

#### 3.1 LIQUID EFFLUENT/WATER ANALYSIS

	DATE: NOVEMBER, 2000			
	1	2	3	4
Date Sampled Installation/Sampling Point Area KADUNA	2/11/2000 REFINERY	9/11/2000 EFFLUENT	6/11/2000	23/11/2000
State KADUNA	ROMI	JUNEAU CALLENDA		
Type of Recipient Environment	KOMI	RIVER		
All Season Discharge rate (m³/day)	FARMING	AND	HABITATION	
Usage Effluent Quantity Discharge (m³/day)		11112		
Characteristics				
pH	10.08	7.43	8.91	9.14
Temperature <sup>0</sup> C	26.6	26.1	28.8	28.7
Turbidity NTU	42	19	31	19
Total Dissolved Solids (TDS) mg/1	518	310	402	306
Suspended Solids	88	30	50	158
Alkalinity P	128.00	NIL	12	28
Alkalinity M	128.00	60.00	84	64
Dissolved Oxygen (DO) mg/1	13.65	8.03	9.92	10.7
Biochemical Oxygen Demand mg/1	616.94	102.67	720	537.50
Chemical Oxygen Demand mg/1	204.46	57.86	101.45	37.74
OH + Grease Content mg/1 Surfactants mg/1	3.01	15.15	7.01	12.8
Phenolic Compounds mg/1	NIL	0.15	0.68	0.08
Salinity as Chloride (Cl') mg/1	38.26	13.87	27.74	22.54
Ammonia (NH <sub>4</sub> <sup>+</sup> ) mg/1	1.15	2.65	2.86	1.41
Anions				
Nitrate (NO <sub>3</sub> -) mg/1	2.94	10.22	8.16	6.5
Phosphate (PO <sub>4</sub> <sup>3</sup> -) mg/1	4.42	5.94	9.03	5.33
Sulphate (SO <sub>4</sub> -) mg/1	-	-	-	-
Sulphide as H <sub>2</sub> S mg/1				
Free CO <sub>2</sub> mg/1	0.6	1.37	1.96	NIL
	-	-	-	<u>.</u>
Bicarbonate (HCO <sub>3</sub> -) mg/1 as CaCO <sub>3</sub> Carbonate (CO <sub>3</sub> <sup>2</sup> -) mg/1 as CaCO <sub>3</sub>	-	-	-	-
Conductivity Carbonate (CO <sub>3</sub> -) mg/1 as CaCO <sub>3</sub>	840	560	- 040	-
Cyanide (ppm)	040	560	840	900
Cyanide (ppin)			<u> -                                     </u>	

#### LIQUID EFFLUENT/WATER ANALYSIS DATE: NOVEMBER, 2000

DATE: NOVEMBER, 2000				
	5			
Date Sampled Installation/Sampling Point Area KADUNA	30/11/2000 REFINERY	EFFLUENT		
State KADUNA Type of Recipient Environment	ROMI	RIVER		
All Season Discharge rate (m³/day) Usage	FARMING	AND	HABITATION	
Effluent Quantity Discharge (m <sup>3</sup> /day)				<u> </u>
<u>Characteristics</u>				
pH	7.07			
Temperature <sup>0</sup> C	28.1			
Turbidity NTU	32			
Total Dissolved Solids (TDS) mg/l	240			
Suspended Solids	24	,	,	
Alkalinity P	NIL 52			
Alkalinity M	11.04			
Dissolved Oxygen (DO) mg/l	360			
Biochemical Oxygen Demand mg/l Chemical Oxygen Demand mg/l	120.32			
OH + Grease Content mg/l	45.7			
Surfactants mg/l				
Phenolic Compounds mg/l	0.23			
Salinity as Chloride (Cl) mg/l	13.87			
Ammonia (NH <sub>4</sub> <sup>+</sup> ) mg/l	0.48			
Anions				
Nitrate (NO <sub>3</sub> -) mg/l	10.00			
Phosphate (PO <sub>4</sub> <sup>3</sup> -) mg/l	7.20			
Sulphate (SO <sub>4</sub> -) mg/l	-			
Sulphide as H <sub>2</sub> S mg/l				
l '	NIL			
Free CO <sub>2</sub> mg/l	-			
Bicarbonate (HCO <sub>3</sub> -) mg/las CaCO <sub>3</sub>	-			
Carbonate (CO <sub>3</sub> <sup>2</sup> -) mg/l as CaCO <sub>3</sub>	-			
Conductivity	420			
Cyanide (ppm)	-			

		1	2	3	4
METALS					
Sodium (Na)	mg/l				A SERVICE SECTION
Potassium (K)	mg/l				Tracerdo autorita
Calcium (Ca)	mg/l				A. Li (2/20/Approximate)
Magnesium (Mg)	mg/l				cardio teccessors of Etc
Lead (Pb)	mg/l				Signification of the second sections in the second sections in the second section in the second section is second section in the section in the second section in the
Cadium (Cd)	mg/l				
Zinc (Zn)	mg/l	NOT	DETERMINED	3	
Copper (Cu)	mg/l				
Chromium (Total)	mg/l				
Chromium (Cr <sup>6+</sup> )	mg/l				
Barium (Ba)	mg/l				
Vanadium (V)	mg/l		·		
Nickel (NI)	mg/l				
Iron (Fe)	mg/l				
Mercury (Hg)	mg/l				

ANALYSIS LABORATORY: WATER SECTION (REF. LAB)

ND - NOT DETERMINED

# LIQUID EFFLUENT/WATER ANALYSIS DATE: NOVEMBER, 2000

DATE: NOVEMBER, 2000		
	1	2
Date Sampled Installation/Sampling Point Area KADUNA State KADUNA	30/11/2000 UPSTREAM	30/11/2000 DOWNSTREAM
Type of Recipient Environment	ROMI	RIVER
All Season Discharge rate (m³/day) Usage	FARMING	AND HABITATION
Effluent Quantity Discharge (m³/day)		
Characteristics pH	6.65	( 00
Temperature <sup>0</sup> C	24.6	6.98
Turbidity NTU	23	23.3
Total Dissolved Solids (TDS) mg/l	74	110
Suspended Solids	20	24
Alkalinity P	NIL	NIL
Alkalinity M	36	46
Dissolved Oxygen (DO) mg/l	11.04	9.95
Biochemical Oxygen Demand mg/l	296.10	275.99
Chemical Oxygen Demand mg/l	184.02	78
OH + Grease Content mg/l	40.9	37.7
Surfactants mg/l	-	_
Phenolic Compounds mg/l	NIL	NIL
Salinity as Chloride (Cl') mg/l	NIL	NIL
Ammonia (NH <sub>4</sub> <sup>+</sup> ) mg/l	0.82	0.74
Anions		
Nitrate (NO <sub>3</sub> -) mg/l	3.4	2.6
Phosphate (PO <sub>4</sub> <sup>3</sup> -) mg/l	2.28	1.47
Sulphate (SO <sub>4</sub> -) mg/l	] -	-
Sulphide as H <sub>2</sub> S mg/l		
Free CO <sub>2</sub> mg/l	0.39	NII.
Bicarbonate (HCO <sub>3</sub> -) mg/l as CaCO <sub>3</sub>	-	- /
Carbonate (CO <sub>3</sub> <sup>2</sup> -) mg/l as CaCO <sub>3</sub>	-	-
Conductivity Carbonate (CO <sub>3</sub> -) mg/l as CaCO <sub>3</sub>	92	280
Cyanide (ppm)	9 <i>L</i>	280
Cyaniae (ppin)	_	

	and the state of t	1	2
<u>METALS</u>			
Sodium (Na)	mg/l		
Potassium (K)	mg/l		
Calcium (Ca)	mg/l		
Magnesium (Mg)	mg/l		
Lead (Pb)	mg/l		
Cadium (Cd)	mg/l		
Zinc (Zn)	mg/l	NOT	DETERMINED
Copper (Cu)	mg/l		
Chromium (Total)	mg/l		
Chromium (Cr <sup>6+</sup> )	mg/l		
Barium (Ba)	mg/l		
Vanadium (V)	mg/l		
Nickel (NI)	mg/l		
Iron (Fe)	mg/l		
Mercury (Hg)	mg/l		

ANALYSIS LABORATORY: WATER LAB SECTION (P)
ND – NOT DETERMINED

#### ANALYSIS REPORT

	RIVER W	VATER	CLARIFII	ER OUTLET	REFINERY EF	FLUENT	
DATA	DATA Design spec.		Design spec.			Design spec.	
					Clear, Colorless		
P <sup>H</sup>	7.0-7.3	7.66	7.0-7		7.0-8.5	7.07	
Electrical conductivity	13-105	90	220(niax.370)			420	
Total solids ppm	38-3,328	88	200(max.350)			264	
Suspended solids	18-3,000	4	20(max.50)		10.0mg\litre	24	
Turbidity	20-3,000	26	20(max.50)		50.0units	32	
Alkalinity (HCO <sub>3</sub> )	20-62	40	62.0			52	
Total Iron ppm	0.02-5.5	-	1.0		0.3 mg\litre	-	
Total Hardness ppm	12.0 -30.0	28	38.0		500.0 mg\litre	32	
Ca Hardness ppm		14				18	
Mg Hardness ppm		14				14	
Chloride ppm	0.2-24.8	NIL	27.8			13.37	
Silica (SiO <sub>2</sub> )	0.8-9.3	24.20	1.7			-	
Sulphate ppm		-	3.0		200.0 mg\litre	-	
Phosphate ppm		2.33				7.20	
B.O.D (5 days) ppm		125.19			25 mg\litre	360	
C.O.D ppm		88	38.40		60.0 mg\litre	120-32	
Settle able Solids	70-326	-			0.3 mg\litre	-	
Total Dissolved Solids		84	.350		2.000.0 mg\litre	240	
Oil		3.88			0.3 mg\litre	45.7	
Hydrocarbons (I.R methods)		-			0.0 mg\litre	•	
Phenols		NIL			0.1 mg\litre	0.23	
Tar					NIL	· · · · · · · · · · · · · · · · · · ·	

	RIVER WATER	CLARIFIER OUTLET	REFINERY EF	FLUENT
DATA	DESIGN SPEC.	DESIGN SPEC.	DESIGN SP	EC.
Ammonia	0.70		1.0mg/Litre as N	0.48
Sulphide as H <sub>2</sub> S	NIL		0.2mg/Litre	NIL
Zinc	-		5.0mg/Litre	-
Lead	-		0.05mg/Litre	-
Arsenic	-		0.05mg/Litre	-
Cyanide	-		0.05mg/Litre	-
Cadmium	-		0.05mg/Litre	-
Boron	-		0.05mg/Litre	_
Vanadium	-		0.05mg/Litre	-
Hexa Chromium	-		0.03mg/Litre	_
Selenium	-		0.01mg/Litre	-
Mercury	-		0.001mg/Litre	-
Temperature	25.4		36 <sup>0</sup> C	28.1
Taste	-		Unobjectionable	-

<sup>0.05</sup>mg/Litre is expected value, 0.1mg/Litre is guaranteed value

# 3.2 LIQUID EFFLUENT/WATER ANALYSIS DATE: AUGUST, 2003

DATE: AUGUST, 2003				
		2	3	<i>;</i>
Date Sampled Installation/Sampling Point Area KADUNA	7/08/2003 REFINERY	14/08/2003 EFFLUENT	21/08/2003	28/08/200
State KADUNA	ROMI	RIVER		
Type of Recipient Environment  All Season Discharge rate (m <sup>3</sup> /day)			,	
Usage	FARMING	AND	HABITATION	
Effluent Quantity Discharge (m³/day)				
Characteristics				
pH	8.24	6.31	6.77	7.58
Temperature <sup>0</sup> C	27.00	26.60	26.60	28.00
Turbidity (NTU)	15.00	14.50	14.00	12.00
Total Dissolved Solids (TDS) mg/l	189.00	234.11	408.25	225.93
Suspended Solids	123.00	160.22	100.42	39.90
Alkalinity P	< 0.01	NIL	NIL	NIL
Alkalinity M	52.00	38.20	24.50	23.30
Dissolved Oxygen (DO) mg/l	7.28	6.70	6.67	7.75
Biochemical Oxygen Demand mg/l	110.25	45.57	88.20	99.96
Chemical Oxygen Demand mg/l	600.00	260.00	140.00	220.00
OH + Grease Content mg/l	ND*	ND*	ND*	ND*
Phenolic Compounds mg/l	0.30	0.49	0.40	0.14
Salinity as Chloride (Cl') mg/l	15.40	16.00	14.80	19.30
Ammonia (NH <sub>4</sub> <sup>+</sup> ) mg/l	1.75	1.68	0.36	0.40
Anions				
Nitrate (NO <sub>3</sub> -) mg/l	1.20	0.70	0.50	0.50
Phosphate (PO <sub>4</sub> <sup>3</sup> -) mg/l	5.23	1.76	9.29	8.83
Sulphate (SO <sub>42</sub> ) mg/l	162.50	215.00	130.00	87.50
Sulphide as H <sub>2</sub> S mg/l	0.04	NIL	NIL	0.04
Conductivity (µs)	657.00	318.00	490.00	405.00
Cyanide (ppm)	ND*	ND*	ND*	ND*
S				
NO+ NOT DECEMBRATION DATE				

ND\* - NOT DETERMINED DUE TO FAULTY EQUIPMENT

			2	3	4
		07/08/2003	14/08/2003	21/08/2003	28/08/2003
<u>METALS</u>					
Sodium (Na)	mg/l	30.96	23.94	33.17	39.22
Potassium (K)	mg/l	ND	ND	ND	ND
Calcium (Ca)	mg/l	ND	ND	ND	ND
Magnesium (Mg)	mg/l	2.68	0.95	2.15	2.62
Lead (Pb)	mg/l	ND	ND	ND	ND
Cadium (Cd)	mg/l	NIL	NIL	NIL	NIL
Zinc (Zn)	mg/l	0.25	0.23	0.11	0.80
Copper (Cu)	mg/l	NIL	NIL	NIL	NIL
Chromium (Total)	mg/l	-	-	_	_
Chromium (Cr <sup>6+</sup> )	mg/l	0.01	NIL	NIL	NIL
Barium (Ba)	mg/l	_	-		-
Vanadium (V)	mg/l	-	_	_	-
Nickel (NI)	mg/l	ND	ND	ND	ND
Iron (Fe)	mg/l	1.70	1.30	1.28	
Mercury (Hg)	mg/l	ND	ND	ND	2.99 ND

ANALYSIS LABORATORY: WATER SECTION (Refinery Laboratory)

ND – NOT DETERMINED DUE TO LAMP FAILURE

# LIQUID EFFLUENT/WATER ANALYSIS DATE: AUGUST, 2003

		and the second s
Date Sampled Installation/Sampling Point ROMI Area KADUNA State KADUNA Type of Recipient Environment All Season Discharge rate (m³/day) Usage Effluent Quantity Discharge (m³/day)	24/08/2003 UPSTREAM KRPC ROMI FARMING	28/08/2003 DOWNSTREAM RIVER AND HABITATION
Characteristics		
pH Temperature <sup>0</sup> C Turbidity (NTU) Total Dissolved Solids (TDS) mg/l Total Hardness mg/l as CaCO <sub>3</sub> Alkalinity P mg/l Alkalinity M mg/l Dissolved Oxygen (DO) mg/l Biochemical Oxygen Demand mg/l Chemical Oxygen Demand mg/l OH + Grease Content mg/l Phenolic Compounds mg/l Salinity as Chloride (Cl') mg/l Ammonia (NH <sub>4</sub> <sup>+</sup> ) mg/l	6.55 27.80 160.00 228.79 20.30 NIL 13.50 7.41 58.80 380.00 ND	5.83 28.00 116.00 216.55 27.50 NIL 6.70 7.76 70.56 319.20 ND 1.29 13.50 1.66
Anions Nitrate (NO <sub>3</sub> -) mg/l Phosphate (PO <sub>4</sub> <sup>3</sup> -) mg/l	0.70 7.56 46.00	NIL 6.93 90.00
Sulphate (SO <sub>4</sub> <sup>2-</sup> ) mg/l Sulphide as H <sub>2</sub> S mg/l Electricity Conductivity (µs) Cyanide (ppm)	0.03 251.30 ND	0.03 394.00 ND
	-1	

ND - NOT DETERMINED DUE TO FAULTY EQUIPMENT

		R-UP	R-DOWN
		1 28/08/2003	2 28/08/2003
<u>METALS</u>			
Sodium (Na) m	g/I	26.30	32.88
Potassium (K) mg	g/l	ND*	ND*
Calcium (Ca) m	g/l	ND*	ND*
Magnesium (Mg) mg	g/l	2.00	2.22
Lead (Pb) mg	g/l	ND*	ND*
Cadium (Cd) mg	g/l	NIL	NIL
Zinc (Zn) mg	y/I	0.32	0.41
Copper (Cu) mg	g/I	NIL	NIL
Chromium (Total) mg	z/l	<u></u>	-
Chromium (Cr <sup>6+</sup> ) mg	<u>1</u> /1	NIL	NIL
Barium (Ba) mg	g/l	-	-
Vanadium (V) mg	<u>z</u> /l	-	-
Nickel (NI) mg	g/I	ND	ND
Iron (Fe) mg	ا/ع	5.10	4.00
Mercury (Hg) mg	<u>4</u> /I	-	-

ANALYSIS LABORATORY: WATER LABORATORY (REFINERY)
ND – NOT DETERMINED DUE TO FAULTY LAMP

#### ANALYSIS REPORT AUGUST, 2003

	RIVER WA		CLARIFIER OUTLET		REFINERY EFFLUENT		
DATA	Design spec.		Design spec.			Design spec.	
					Clear, Colorless		
$P^{H}$	7.0-7.3	6.76	7.0-7		7.0-8.5	7.58	
Electrical conductivity (µs)	13-105	45.40	220(max.370)			405.00	
Total solids ppm	38-3,328	274.23	200(max.350)			265.83	
Suspended solids PPM	18-3,000	41.13	20(max.50)		10.0mg\litre	39.90	
Turbidity (NTU)	20-3,000	290.00	20(max.50)		50.0units	12.00	
Alkalinity M ppm	20-62	17.40	62.0			23.30	
Total Iron ppm	0.02-5.5	13.89	1.0		0.3 mg\litre	2.99	
Total Hardness ppm	12.0 -38.0	16.40	38.0		500.0 mg\litre	28.60	
Ca Hardness ppm		10.10				18.00	
Mg Hardness ppm		6.30				10.60	
Chloride ppm	0.2-24.8	7.40	27.8			19.30	
Silica (SiO <sub>2</sub> )	0.8-9.3	13.05	1.7			-	
Sulphate ppm		9.00	3.0		200.0 mg\litre	87.50	
Phosphate ppm		22.97				3.83	
B.O.D (5 days) ppm		29.40			25 mg\litre	99.96	
C.O.D ppm		212.80	38.40		60.0 mg\litre	220.00	
Settle able Solids		-			0.3 mg\litre	-	
Total Dissolved Solids ppm	70-326	233.10	.350		2.000.0 mg\litre	225.93	
Oil		ND*			0.3 mg\litre	ND	
Hydrocarbons (I.R methods)		-			0.0 mg\litre	-	
Phenols ppm		0.10			0.1 mg\litre	0.14	
Dissolved Oxygen		7.07			NIL	7.75	

ND - NOT DETERMINED DUE TO FAULTY EQUIPMENT.

	RIVER WATER	CLARIFIER OUTLET	REFINERY EF	FLUENT
DATA (mg/l)	DESIGN SPEC.	DESIGN SPEC.	DESIGN SI	PEC.
Ammonia - N	1.48		1.0mg/Litre as N	0.40
Sulphide as H <sub>2</sub> S	0.05		0.2mg/Litre	0.04
Zinc	0.30		5.0mg/Litre	0.80
Lead	ND		0.05mg/Litre	ND
Arsenic	-		0.05mg/Litre	-
Cyanide	ND		0.05mg/Litre	NIL
Cadmium	NIL		0.05mg/Litre	
Boron	-		0.05mg/Litre	
Vanadium	-		0.05mg/Litre	
Hexa Chromium	NIL		0.03mg/Litre	NIL
Selenium	-		0.01mg/Litre	-
Mercury	ND		0.001mg/Litre	ND
Temperature ( <sup>0</sup> C)	26.80		36 <sup>0</sup> C	28.00
Taste			Unobjectionable	-

0.05mg/Litre is expected value, 0.1mg/Litre is guaranteed value. ND\* - NOT DETERMINED DUE TO FAULTY EQUIPMENT.

# 3.3 LIQUID EFFLUENT/WATER ANALYSIS DATE: MAY, 2004

DATE: MAY, 2004				
	1	2	3	4
	6/5/2004	13/5/2004	20/5/2004	27/5/2004
Date Sampled Installation/Sampling Point Area KADUNA	REFINERY	EFFLUENT		
State KADUNA				
Type of Recipient Environment	ROMI	RIVER		
All Season Discharge rate (m <sup>3</sup> /day)				
Usage	FARMING	AND	HABITATION	
Effluent Quantity Discharge (m³/day)			,	
Characteristics				
pH	7.36	2.85	6.09	5.54
Temperature <sup>0</sup> C	29.2	29.1	29.4	29.1
Turbidity (NTU)	22	21	16	80
Total Dissolved Solids (TDS) mg/l	437.71	467.57	410.85	321.94
Suspended Solids	38.29	35.43	41.22	54.32
Alkalinity P mg/l	NIL	NIL	NIL	NIL
Alkalinity M mg/l	60.00	84.00	67.00	44
Dissolved Oxygen (DO) mg/l	6.80	6.90	8.16	267.62
Biochemical Oxygen Demand mg/l	179.34	14.70	199.90	72.99
Chemical Oxygen Demand mg/l	360.00	46.16	203.08	120.99
OH + Grease Content mg/l	ND*	ND*	ND*	ND*
Phenolic Compounds mg/l	0.55	0.49	0.36	0.16
Salinity as Chloride (Cl') mg/l	27.80	31.60	18.30	20.8
Ammonia (NH <sub>4</sub> <sup>+</sup> ) mg/l	0.92	0.66	0.33	1.25
Anions				
Nitrate (NO <sub>3</sub> -) mg/l	1.10	0.40	0.50	0.50
Phosphate (PO <sub>4</sub> <sup>3</sup> -) mg/l	6.87	3.25	0.92	13.50
Sulphate (SO <sub>42</sub> ) mg/l	42.00	165.00	200.00	90,00
Sulphide as H <sub>2</sub> S mg/l	0.01	0.01	0.07	0.013
Conductivity (µs)	342	1048	832	577
Cyanide (ppm)	ND*	ND*	ND*	ND*
LIOUID FEEL HENTAVATED AN				

LIQUID EFFLUENT/WATER ANALYSIS – MAY 2004

ND\* - NOT DETERMINED DUE TO FAULTY EQUIPMENT

				T	
		1	201515000	3	4
		6/5/2004	13/5/2004	20/5/2004	27/5/2004
<u>METALS</u>					
Sodium (Na)	mg/l	ND*	ND*	ND*	ND*
Potassium (K)	mg/l	ND*	ND*	ND*	ND*
Calcium (Ca)	mg/l	ND*	ND*	ND*	ND*
Magnesium (Mg)	mg/l	ND*	ND*	ND*	ND*
Lead (Pb)	mg/l	ND*	ND*	ND*	ND*
Cadium (Cd)	mg/l	ND*	ND*	ND*	ND*
Zinc (Zn)	mg/l	ND*	ND*	ND*	ND*
Copper (Cu)	mg/l	ND*	ND*	ND*	ND*
Chromium (Total)	mg/l	ND*	ND*	ND*	ND*
Chromium (Cr <sup>6+</sup> )	mg/i	ND*	ND*	ND*	ND*
Barium (Ba)	mg/l	ND*	ND*	ND*	ND*
Vanadium (V)	mg/l	ND*	ND*	ND*	ND*
Nickel (NI)	mg/l	ND*	ND*	ND*	ND*
Iron (Fe)	mg/l	ND*	ND*	ND*	ND*
Mercury (Hg)	mg/l	ND*	ND*	ND*	ND*

ND – NOT DETERMINED DUE TO LAMP FAILURE AND ALSO, FAULTY EQUIPMENT

ANALYSIS LABORATORY: WATER SECTION (Refinery Laboratory)

# LIQUID EFFLUENT/WATER ANALYSIS DATE: AUGUST, 2003

Date Sampled Installation/Sampling Point ROMI Area KADUNA State KADUNA	27/5/2004 UPSTREAM KRPC	27/5/2004 DOWNSTREAM
Type of Recipient Environment	ROMI	RIVER
All Season Discharge rate (m³/day)		
Usage	FARMING	AND HABITATION
Effluent Quantity Discharge (m <sup>3</sup> /day)		
Characteristics		
рН	66.0	6.47
Temperature <sup>0</sup> C	27.5	28.9
Turbidity (NTU)	450.00	270.00
Total Dissolved Solids (TDS) mg/l	95.49	49.65
Total Hardness mg/l as CaCO <sub>3</sub>	17.60	31.40
Alkalinity P mg/l	NIL	NIL
Alkalinity M mg/l	29	43
Dissolved Oxygen (DO) mg/l	6.80	7.34
Biochemical Oxygen Demand mg/l	26.16	98.49
Chemical Oxygen Demand mg/l	-	36.50
OH + Grease Content mg/l	ND*	ND*
Surfactants mg/l	<0.01 12.60	0.04
Phenolic Compounds mg/l	1.44	19.90
Ammonia (NH <sub>4</sub> <sup>+</sup> ) mg/l	1.44	2.20
Anions		
Nitrate (NO <sub>3</sub> -) mg/l	2.60	0.90
Phosphate Sulphate (PO <sub>4</sub> <sup>3</sup> -) mg/l	32.10	18.01
Sulphate (SO <sub>4</sub> <sup>2</sup> ) mg/l	NIL	25.00
Sulphide as H <sub>2</sub> S mg/l	0.05	0.03
	79.60	425
Electricity Conductivity (µs) Cyanide (ppm)	ND	ND
Cyamuc (ppm)		
ALD ALOND DESIGNATION AND ASSESSED TO		

ND - NOT DETERMINED DUE TO FAULTY EQUIPMENT

			R-UP	R-DO	WN
				1 27/5/2004	2 27/5/2004
METALS					
Sodium	(Na)	mg/l		ND*	ND*
Potassium	(K)	mg/l		ND*	ND*
Calcium	(Ca)	mg/l		ND*	ND*
Magnesium	(Mg)	mg/l		ND*	ND*
Lead	(Pb)	mg/l		ND*	ND*
Cadium	(Cd)	mg/l		ND*	ND*
Zinc	(Zn)	mg/l		ND*	ND*
Copper	(Cu)	mg/l		ND*	ND*
Chromium	(Total)	mg/l		ND*	ND*
Chromium	(Cr <sup>6+</sup> )	mg/l		ND*	ND*
Barium	(Ba)	mg/l		ND*	ND*
Vanadium	(V)	mg/l		ND*	ND*
Nickel	(NI)	mg/l		ND*	ND*
lron	(Fe)	mg/l		ND*	ND*
Mercury	(Hg)	mg/l		ND*	ND*

ANALYSIS LABORATORY: WATER SECTION (REFINERY LAB)

ND - NOT DETERMINED DUE TO FAULTY LAMP

# ANALYSIS REPORT MAY, 2003

	RIVER WATER		CLARIFI	ER OUTLET	REFINERY EFFLUENT		
DATA	Design	spec.	Desi	ign spec.		Design spec.	
					Clear, Colorless		
$P^{H}$	7.0-7.3	7.17	7.0-7		7.0-8.5	5.54	
Electrical conductivity (µs)	13-105	55.10	220(max.370)			577.00	
Total solids ppm	38-3,328	497.59	200(max.350)			321.94	
Suspended solids PPM	18-3,000	73.58	20(max.50)		10.0mg\litre	54.32	
Turbidity (NTU)	20-3,000	480	20(max.50)		50.0units	80.00	
Alkalinity M ppm	20-62	35	62.0			44.00	
Total Iron ppm	0.02-5.5	ND*	1.0		0.3 mg\litre	ND*	
Total Hardness ppm	12.0 -38.0	16.70	38.0		500.0 mg\litre	48.50	
Ca Hardness ppm		11.50				27.20	
Mg Hardness ppm		5.20				21.30	
Chloride ppm	0.2-24.8	10.60	27.8			20.80	
Silica (SiO <sub>2</sub> )	0.8-9.3	15.28	1.7			-	
Sulphate ppm		NIL	3.0		200.0 mg\litre	90.00	
Phosphate ppm		79.58				13.50	
B.O.D (5 days) ppm		20.58			25 mg\litre	72.99	
C.O.D ppm		-	38.40		60.0 mg\litre	120.54	
Settle able Solids		-			0.3 mg\litre	-	
Total Dissolved Solids ppm	70-326	424.01	.350		2.000.0 mg\litre	267.62	
Oil		ND*			0.3 mg\litre	ND*	
Hydrocarbons (I.R methods)		-	·		0.0 mg\litre	ND	
Phenols ppm		<0.01			0.1 mg\litre	0.16	
Dissolved Oxygen		6.66			NIL	7.09	

ND - NOT DETERMINED DUE TO FAULTY EQUIPMENT.

	RIVER WATER	CLARIFIER OUTLET	REFINERY EFI	FLUENT
DATA (mg/l)	DESIGN SPEC.	DESIGN SPEC.	DESIGN SPEC.	
Ammonia - N	3.25		1.0mg/Litre as N	1.25
Sulphide as H <sub>2</sub> S	0.11		0.2mg/Litre	0.01
Zinc	ND*		5.0mg/Litre	ND*
Lead	ND*		0.05mg/Litre	ND*
Arsenic	NIL		0.05mg/Litre	ND*
Cyanide	ND*	*	0.05mg/Litre	ND*
Cadmium	ND*		0.05mg/Litre	ND*
Boron	ND*		0.05mg/Litre	ND*
Vanadium	ND*		0.05mg/Litre	ND*
Hexa Chromium	NIL		0.03mg/Litre	NIL
Selenium	-		0.01mg/Litre	-
Mercury			0.001 mg/Litre	_
Temperature ( <sup>0</sup> C)	28.9		36 <sup>0</sup> C	29.1
Taste	-		Unobjectionable	-

0.05mg/Litre is expected value, 0.1mg/Litre is guaranteed value. ND\* - NOT DETERMINED DUE TO FAULTY EQUIPMENT.

### 3.4 METHODOLOGY

1. Procedure for the analysis of Total Suspended Dissolved Solids (TSS).

100ml of water sample was filtered through fibre glass filter, the filter was placed in an evaporating dish and dried in the oven at temperature of about 105°C for one hour. The fibre glass intermittently and dried repeatedly till a constant weight was obtained.

 $(A - B) \times 100$  volume of water sample.

Where A=weight of filter + residue

B=weight of filter only

Total dissolved solids is given by the equation

2. Procedure for the analysis of Turbidity.

Turbidity was determined using attach turbid meter, the meter was calibrated for operation and the standard supplied with the unit were checked. The appropriate range was selected (100NTU). The cell riser was properly installed in the cell holder. The cell sample was filled with 25ml of sample being tested and covered inside the instrument. The meter readings were recorded.

3. Procedure for analysis of Temperature

Temperatures were determined using a mercury –glass thermometer of range 10<sup>o</sup>C-50<sup>o</sup>C. The thermometer was placed at a depth of about 15cm for five minutes before taking reading.

4. Procedure for analysis of pH

pH was determined with Beckam Electric pH meter model H%. The reference electrode was standardized before use. The pH meter was kept on for about 2 hours to warm the

equipment. The green bulb was cleaned repeatedly with fresh distilled water and the Temperature of the instrument was adjusted to the room Temperature.

5. Procedure for the analysis of Dissolved oxygen (DO).

Oxygen was determined by Winkler Titrimetric method. The sample was acidified by adding 1ml of concentrated H<sub>2</sub>SO<sub>4</sub> and then shaken properly. 100ml of the sample was introduced into a beaker, 5 drops of starch was also added.

Dissolved Oxygen in the sample was titrated using Na<sub>2</sub>SO<sub>4</sub>.5H<sub>2</sub>O until a pale straw or colourless solution was obtained within 2 minutes.

The amount of Dissolved Oxygen in mg/l is given by the equation

Titrants Vol. x 1000 Vol. of water sample x Vol. of sample bottle

6. Biochemical Oxygen Demand's Procedure.

The diluted water was pre-treated followed by pre-treatment of sample. The samples were kept in the water- cooled incubator; at room Temperature before dilution. All samples were well mixed before dilution.

7. Procedure for Analysis of Total Dissolved Solids (TDS).

Total Dissolved Solid was determined by Wrinkle's method. 10ml of the sample was weighed inside a crucible. The sample was dried in a steam bath and dried completely in an oven. The dried crucible was weighed when cold.

TDS mg/l = Initial weight of crucible + sample - Final weight after drying.

## CHAPTER FOUR.

# 4.0 MODEL DEVELOPMENT.

# 4.1 MODELING FOR LIQUID EFFLUENT USING pH AS DEPENDENT VARIABLE.

Modeling for Liquid effluent using pH as the optimization criteria (dependent variable).

The pH of liquid effluent is dependent upon certain parameters present in the waste water, such as temperature, biochemical oxygen demand (BOD), heavy metal e.t.c. Mathematically, pH is represented as:

In this model, the parameters considered include Temperature, Turbidity, TDS, Dissolved Oxygen (DO), BOD, CO, Nitrate, Phosphate, Sulphate, Sulphide.

Let Temperature = T; Turbidity = U; TDS = D; Dissolved Oxygen = O;

Biochemical Oxygen Demand = B; Chemical Oxygen Demand = C;

Nitrate = N; Phosphate = P; and Sulphate = S.

Therefore, the pH can be written as:

$$pH = f(aT + bU + cD + dO + eB + fC + gN + hP + iS)$$
----(2)

where, pH is the dependent variable in the equation, T,U,D,O,B,C,N,P,S are the independent variables, a,b,c,d,e,f,g,h,i are the constants.

Letting I to represent the square of the difference between the values of observed pH and its modeled values (pH model) i.e.

$$I = [pH - (aT + bU + cD + dO + eB + fC + gN + hP + iS)]^{2}$$
(3)

For m experimental values,

$$mI = \sum [pH_I - aT_I - bU_I - cD_I - dO_I - eB_I - fC_I - gN_I - hP_I - iS_I]^2$$
-----(4)

In order to minimize ml with respect to the coefficients, using the first partial derivatives of ml and equating these to zero, the necessary minimum conditions can be obtained. i.e. from equation (4) we have;

$$\frac{\delta(mI)}{\delta a} = -2 \sum_{i=1}^{n} \left[ pH_{i} - aT_{i} - bU_{i} - cD_{i} - dO_{i} - eB_{i} - fC_{i} - gN_{i} - hP_{i} - iS_{i} \right]^{2} = 0 ----(5)$$

$$\frac{\delta(mI)}{\delta h} = -2 \Sigma U_{I} [pH_{I} - aT_{I} - bU_{I} - cD_{I} - dO_{I} - eB_{I} - fC_{I} - gN_{I} - hP_{I} - iS_{I}]^{2} = 0 -----(6)$$

$$\frac{\delta(mI)}{\delta c} = -2 \sum_{i} \left[ pH_{i} - aT_{i} - bU_{i} - cD_{i} - dO_{i} - eB_{i} - fC_{i} - gN_{i} - hP_{i} - iS_{i} \right]^{2} = 0 -----(7)$$

$$\frac{\delta(ml)}{\delta d} = -2 \sum_{i=1}^{n} \left[ pH_{i} - aT_{i} - bU_{i} - cD_{i} - dO_{i} - eB_{i} - tC_{i} - gN_{i} - hP_{i} - iS_{i} \right]^{2} = 0 ----(8)$$

$$\frac{\delta(mI)}{\delta e} = -2 \; \mathbf{\Sigma} B_{\mathbf{I}} \left[ pH_{\mathbf{I}} - aT_{\mathbf{I}} - bU_{\mathbf{I}} - cD_{\mathbf{I}} - dO_{\mathbf{I}} - eB_{\mathbf{I}} - fC_{\mathbf{I}} - gN_{\mathbf{I}} - hP_{\mathbf{I}} - iS_{\mathbf{I}} \right]^2 = 0 \; -----(9)$$

$$\frac{\delta(mI)}{\delta f} = -2 \sum_{i} \left[ pH_{I} - aT_{I} - bU_{I} - cD_{I} - dO_{I} - eB_{I} - fC_{I} - gN_{I} - hP_{I} - iS_{I} \right]^{2} = 0 ----(10)$$

$$\frac{\delta(mI)}{\delta g} = -2 \sum_{I} \left[ pH_{I} - aT_{I} - bU_{I} - cD_{I} - dO_{I} - eB_{I} - fC_{I} - gN_{I} - hP_{I} - iS_{I} \right]^{2} = 0 ----(11)$$

$$\frac{\delta(mI)}{\delta h} = -2 \sum_{i=1}^{n} [pH_{i} - aT_{i} - bU_{i} - cD_{i} - dO_{i} - eB_{i} - fC_{i} - gN_{i} - hP_{i} - iS_{i}]^{2} = 0 ----(12)$$

$$\frac{\delta(mI)}{\delta i} = -2 \sum_{I} [pH_{I} - aT_{I} - bU_{I} - cD_{I} - dO_{I} - eB_{I} - fC_{I} - gN_{I} - hP_{I} - iS_{I}]^{2} = 0 ----(13)$$

equations (5)-(13) can be arranged to give:

$$\frac{\delta(mI)}{\delta a} = \sum_{i=1}^{n} \left[ pH_{i} - aT_{i} - bU_{i} - cD_{i} - dO_{i} - eB_{i} - fC_{i} - gN_{i} - hP_{i} - iS_{i} \right] = -2 \times 0$$

which can be written as:

$$\Sigma T_1[pH_1 - aT_1 - bU_1 - cD_1 - dO_1 - eB_1 - fC_1 - gN_1 - hP_1 - iS_1] = 0$$

Expanding the bracket gives:

$$\Sigma T_1 pH_1 - a \Sigma T_1^2 - b \Sigma T_1U_1 - c \Sigma T_1D_1 - d \Sigma T_1O_1 - e \Sigma T_1B_1 - f \Sigma T_1C_1 - g \Sigma T_1N_1 - h \Sigma T_1P_1 - i \Sigma T_1S_1] = 0$$
 ----(14)

from equation (14), making  $\Sigma T_1$  pH<sub>1</sub>the subject of the formula, we have:

$$\Sigma T_I pH_I = a \Sigma T^2_I + b \Sigma T_I U_I + c \Sigma T_I D_I + d \Sigma T_I O_I + e \Sigma T_I B_I + f \Sigma T_I C_I + g \Sigma T_I N_I + h \Sigma T_I P_I + i \Sigma T_I S_I -----(15)$$

applying the technique to the other equations (6)-(13), we obtain:

$$\Sigma D_{I} pH_{I} = a \Sigma D_{I}I_{I} + b \Sigma D_{I}U_{I} + c \Sigma D_{I}^{2}I_{I} + d \Sigma D_{I}O_{I} + e \Sigma D_{I}B_{I} + f \Sigma D_{I}C_{I} + g \Sigma D_{I}N_{I} + b \Sigma D_{I}P_{I} + i \Sigma D_{I}S_{I}$$
 (17)

$$\Sigma O_{I} pH_{I} = a \Sigma O_{I}I_{I} + b \Sigma O_{I}U_{I} + c \Sigma O_{I}D_{I} + d \Sigma O_{I}^{2}I_{I} + e \Sigma O_{I}B_{I} + f \Sigma O_{I}C_{I} + g \Sigma O_{I}N_{I} + h \Sigma O_{I}P_{I} + i \Sigma O_{I}S_{I}$$

$$\begin{split} & \Sigma C_I pH_I = a \Sigma C_I I_I + b \Sigma C_I U_I + + c \Sigma C_I D_I + d \Sigma C_I O_I + e \Sigma C_I B_I + f \Sigma C_I^2 + g \Sigma C_I N_I \\ & + h \Sigma C_I P_I + i \Sigma C_I S_I -----(20) \end{split}$$

$$\Sigma N_{I} p H_{I} = a \Sigma N_{I} I_{I} + b \Sigma N_{I} U_{I} + c \Sigma N_{I} D_{I} + d \Sigma N_{I} O_{I} + e \Sigma N_{I} B_{I} + f \Sigma N_{I} C_{I} + g \Sigma N_{I}^{2} I_{I} + h \Sigma N_{I} P_{I} + i \Sigma N_{I} S_{I}$$

$$\begin{split} &\Sigma S_{I} \ pH_{I} = a \ \Sigma S_{I} I_{I} + b \ \Sigma S_{I} U_{I} + c \ \Sigma S_{I} D_{I} + d \ \Sigma S_{I} O_{I} + e \ \Sigma S_{I} B_{I} + f \ \Sigma S_{I} C_{I} + g \ \Sigma S_{I} N_{I} + h \ \Sigma S_{I} P_{I} + i \ \Sigma P^{2}_{I} ------(23) \end{split}$$

Where 
$$\Sigma = \sum_{ii=1}^{n}$$
 where  $n = 6$ . The summation was obtained from the data using MathCAD.

Applying the formula,  $t^1 = 1$ . Solve (Z, z) s MathCAD programming language used in solving two matrices to a solution.

data :=				y#************************************						
	0	1	2	3	4	5	6	7	8	9
0	10.08	26.6	42	518	13.65	616.94	204.46	2.94	4.42	0.6
	7.43	26.1	19	310	8.03	102.67	57. <b>8</b> 6	10.22	5.94	1.37
2	8.91	28.8	31	402	9.92	720	101.45	8.16	9.03	1.96
3	9.14	28.7	19	306	10.7	537.5	37.74	6.5	5.38	0
4	6.65	24.6	23	74	11.04	296.19	184.02	3.4	2.28	0.39
5	6.98	25.3	22	110	9.95	275.99	78	2.6	1.47	0
pH:= data $\langle S \rangle$ B:= data $\langle S \rangle$ $\sum (T^2) = 4287.15$ $\sum (T \cdot H) = 6952$ $\sum (T \cdot H) = 1172$ $\sum (U \cdot O) = 1762$ $\sum (D \cdot N) = 1062$ $\sum (O \cdot U) = 1762$ $\sum (O \cdot C) = 7422$ $\sum (B \cdot T) = 6952$	(o) 21.362 .759 .99.51 .43	$T := dat$ $C := dat$ $\sum (T \cdot U)$ $\sum (U \cdot I)$ $\sum (U \cdot I)$ $\sum (D \cdot I)$ $\sum (O \cdot I)$ $\sum (O \cdot I)$	a ⟨1⟩ a ⟨6⟩  ⇒ ⟨6⟩  ⇒ ⟨1⟩  ⇒ ⟨1⟩  = 4173.  ⇒ (1) = 4173.  ⇒ (1) = 120.9  ⇒ (1) = 120.9  ⇒ (2) = 1873.  ⇒ (3) = 7327.  ⇒ (4) = 1873.  ⇒ (5) = 1873.  ⇒ (7) = 1873.  ⇒ (8) = 336.	U:= N:= 6 8.86 96 33.5 72	data (2) $ \frac{1}{2} $	$D:= P:= \longrightarrow P:= A60$ $\longrightarrow N) = 915.$	= data (3) = data (8) 833 924 97.13 33 594.58 4 .972	$\begin{array}{c} O_{2} \\ & \text{H}_{2} \\ & \sum_{\overline{C}} \overline{C} \\ & $	= data	\$\cdot\\$\
$\sum \overline{\left( \mathbf{B}^2 \right)} = 136236$					$\sum_{B}$	→ N) = 139	956.661		$\rightarrow 3 \cdot P = 1$	
$\sum \overrightarrow{(B \cdot H)} = 203$	37.536	$\sum \overline{(C \cdot )}$	→ (T) = 1745	3.972	$\sum_{C} \overline{C}$	→ U) = 194	197.13	$\sum_{i}$	<del>· · · · · · · · · · · · · · · · · · · </del>	198375.7
					20					

pH T U D O B C N P H

$$\sum \overrightarrow{(C \cdot O)} = 7473.378 \qquad \sum \overrightarrow{(C \cdot B)} = 301441.392 \qquad \sum \overrightarrow{(C^2)} = 96815.442 \qquad \sum \overrightarrow{(C \cdot N)} = 3094.052$$

$$\sum \overrightarrow{(C \cdot P)} = 2900.762 \qquad \sum \overrightarrow{(C \cdot II)} = 472.554 \qquad \sum \overrightarrow{(N \cdot T)} = 915.924 \qquad \sum \overrightarrow{(N \cdot U)} = 829.52$$

$$\sum \overrightarrow{(N \cdot D)} = 10498.04 \qquad \sum \overrightarrow{(N \cdot O)} = 336.101 \qquad \sum \overrightarrow{(N \cdot B)} = 13956.661 \qquad \sum \overrightarrow{(N \cdot C)} = 3094.052$$

$$\sum \overrightarrow{(N^2)} = 240.248 \qquad \sum \overrightarrow{(N \cdot P)} = 193.93 \qquad \sum \overrightarrow{(N \cdot II)} = 33.085 \qquad \sum \overrightarrow{(P \cdot T)} = 780.355$$

$$\sum \overrightarrow{(P \cdot U)} = 765.43 \qquad \sum \overrightarrow{(P \cdot D)} = 9737.72 \qquad \sum \overrightarrow{(P \cdot O)} = 294.972 \qquad \sum \overrightarrow{(P \cdot B)} = 13811.103$$

$$\sum \overrightarrow{(P \cdot C)} = 2900.762 \qquad \sum \overrightarrow{(P \cdot N)} = 193.93 \qquad \sum \overrightarrow{(P^2)} = 172.665 \qquad \sum \overrightarrow{(P \cdot II)} = 29.378$$

$$\sum \overrightarrow{(II \cdot T)} = 117.759 \qquad \sum \overrightarrow{(II \cdot U)} = 120.96 \qquad \sum \overrightarrow{(II \cdot D)} = 1552.28 \qquad \sum \overrightarrow{(II \cdot O)} = 42.94$$

$$\sum \overrightarrow{(II \cdot P)} = 2037.536 \qquad \sum \overrightarrow{(P \cdot I)} = 1321.161 \qquad \sum \overrightarrow{(PI \cdot I)} = 1320.91 \qquad \sum \overrightarrow{(PI \cdot D)} = 15163.3$$

$$\sum \overrightarrow{(PI \cdot O)} = 526.307 \qquad \sum \overrightarrow{(PI \cdot I)} = 36.284$$

$$Z = \begin{pmatrix} 4287.15 & 4173.6 & 46833 & 1688.778 & 69521.362 & 17453.972 & 915.924 & 780.355 & 117.759 \\ 4173.6 & 4460 & 50044 & 1709.51 & 73278.86 & 19497.13 & 829.52 & 765.43 & 120.96 \\ 46833 & 50044 & 637240 & 18733.5 & 857594.58 & 198375.7 & 10498.04 & 9737.72 & 1552.28 \\ 1688.778 & 1709.51 & 18733.5 & 684.584 & 28155.359 & 7473.378 & 336.101 & 294.972 & 42.94 \\ 69521.362 & 73278.86 & 857594.58 & 28155.359 & 1362361.339 & 301441.392 & 13956.661 & 13811.103 & 2037.536 \\ 17453.972 & 19497.13 & 198375.7 & 7473.378 & 301441.392 & 96815.442 & 3094.052 & 2900.762 & 472.554 \\ 915.924 & 829.52 & 10498.04 & 336.101 & 13956.661 & 3094.052 & 240.248 & 193.93 & 33.085 \\ 780.355 & 765.43 & 9737.72 & 294.972 & 13811.103 & 2900.762 & 193.93 & 172.665 & 29.378 \\ 117.759 & 120.96 & 1552.28 & 42.94 & 2037.536 & 472.554 & 33.085 & 29.378 & 6.231 \end{pmatrix}$$

$$\sum \overrightarrow{(pH \cdot T)} = 1321.161$$

$$\sum \overrightarrow{(pH \cdot D)} = 15163.3$$

$$\sum \overrightarrow{(pH \cdot D)} = 15163.3$$

$$\sum \overrightarrow{(pH \cdot D)} = 22205.617$$

$$\sum \overrightarrow{(pH \cdot P)} = 243.741$$

$$\sum \overrightarrow{(pH \cdot H)} = 36.284$$

$$z := \begin{pmatrix} \sum (\overline{pH \cdot T}) \\ \sum (\overline{pH \cdot U}) \\ \sum (\overline{pH \cdot D}) \\ \sum (\overline{pH \cdot D}) \\ \sum (\overline{pH \cdot D}) \\ \sum (\overline{pH \cdot P}) \\ \sum (\overline{pH \cdot P}) \\ \sum (\overline{pH \cdot H}) \end{pmatrix}$$

$$Z = \begin{pmatrix} 1321.161 \\ 1320.91 \\ 15163.3 \\ 526.307 \\ 22205.617 \\ 5507.893 \\ 278.443 \\ 243.741 \\ 36.284 \end{pmatrix}$$

t' := lsolve(Z, z)

 $pH_{m} := 0.329 \cdot T - 0.241 \cdot U + 0.014 \cdot D + 0.423 \cdot O - 0.00106 \cdot B + 0.001044 \cdot C - 0.592 \cdot N - 0.004394 \cdot P + 1.421 \cdot H$  SIMULATION

$$pH_{m} = \begin{pmatrix} 10.308 \\ 7.567 \\ 9.086 \\ 9.271 \\ 6.666 \\ 7.014 \end{pmatrix}$$

error :=  $pH - pH_m$ 

error = 
$$\begin{pmatrix} -0.228 \\ -0.137 \\ -0.176 \\ -0.131 \\ -0.016 \\ -0.034 \end{pmatrix}$$

$$\%error := \overline{\left(\frac{error}{pH} \cdot 100\right)}$$

$$\%error = \begin{pmatrix} -2.257 \\ -1.838 \\ -1.973 \\ -1.438 \\ -0.238 \\ -0.484 \end{pmatrix}$$

$$\overrightarrow{(T^2)} = \begin{pmatrix}
707.56 \\
681.21 \\
829.44 \\
823.69 \\
605.16 \\
640.09
\end{pmatrix}$$

$$\overrightarrow{(T \cdot U)} = \begin{pmatrix}
1117.2 \\
495.9 \\
892.8 \\
545.3 \\
565.8 \\
556.6
\end{pmatrix}$$

$$\overrightarrow{(T \cdot D)} = \begin{pmatrix}
13778.8 \\
8091 \\
11577.6 \\
8782.2 \\
1820.4 \\
2783
\end{pmatrix}$$

$$\overrightarrow{(T \cdot O)} = \begin{pmatrix}
363.09 \\
209.583 \\
285.696 \\
307.09 \\
271.584 \\
251.735
\end{pmatrix}$$

$$\overrightarrow{(T \cdot D)} = (\overrightarrow{T \cdot D}) = 4287.15$$

$$\overrightarrow{(T \cdot D)} = 4287.15$$

$$\overrightarrow{(T \cdot D)} = 46833$$

$$\overrightarrow{(T \cdot D)} = 1688.778$$

$$\overrightarrow{(T \cdot D)} = \begin{pmatrix} 13778.8 \\ 8091 \\ 11577.6 \\ 8782.2 \\ 1820.4 \\ 2783 \end{pmatrix}$$

$$(T \cdot O) = \begin{pmatrix} 30.583 \\ 209.583 \\ 285.696 \\ 307.09 \\ 271.584 \\ 251.735 \end{pmatrix}$$

$$\overrightarrow{\Gamma^2} = 4287.15$$

$$\sum \overrightarrow{(T \cdot U)} = 4173.6$$

$$\sum \overrightarrow{(T \cdot D)} = 4683$$

$$\sum \overrightarrow{(T \cdot O)} = 1688.778$$

$$\overrightarrow{(T \cdot B)} = \begin{pmatrix} 16410.604 \\ 2679.687 \\ 20736 \\ 15426.25 \\ 7286.274 \\ 6982.547 \end{pmatrix} \qquad \overrightarrow{(T \cdot C)} = \begin{pmatrix} 5438.636 \\ 1510.146 \\ 2921.76 \\ 1083.138 \\ 4526.892 \\ 1973.4 \end{pmatrix} \qquad \overrightarrow{(T \cdot N)} = \begin{pmatrix} 78.204 \\ 266.742 \\ 235.008 \\ 186.55 \\ 83.64 \\ 65.78 \end{pmatrix} \qquad \overrightarrow{(T \cdot P)} = \begin{pmatrix} 117.572 \\ 155.034 \\ 260.064 \\ 154.406 \\ 56.088 \\ 37.191 \end{pmatrix}$$

$$\overrightarrow{(T \cdot C)} = \begin{pmatrix} 5438.636 \\ 1510.146 \\ 2921.76 \\ 1083.138 \\ 4526.892 \\ 1973.4 \end{pmatrix}$$

$$(T \cdot N) = \begin{pmatrix} 78.204 \\ 266.742 \\ 235.008 \\ 186.55 \\ 83.64 \\ 65.78 \end{pmatrix}$$

$$\overrightarrow{(T \cdot P)} = \begin{pmatrix} 155.034 \\ 155.034 \\ 260.064 \\ 154.406 \\ 56.088 \\ 37.191 \end{pmatrix}$$

$$\sum \overrightarrow{(T \cdot B)} = 69521.362$$

$$\overrightarrow{\sum(T\cdot C)} = 17453.972$$

$$\sum \overrightarrow{(T \cdot N)} = 915.924$$

$$\overrightarrow{\Gamma(T \cdot P)} = 780.355$$

$$\overrightarrow{(T \cdot H)} = \begin{pmatrix} 15.96 \\ 35.757 \\ 56.448 \\ 0 \\ 9.594 \\ 0 \end{pmatrix} \qquad \overrightarrow{(U \cdot T)} = \begin{pmatrix} 1117.2 \\ 495.9 \\ 892.8 \\ 545.3 \\ 565.8 \\ 556.6 \end{pmatrix} \qquad \overrightarrow{(U^2)} = \begin{pmatrix} 1764 \\ 361 \\ 961 \\ 361 \\ 529 \\ 484 \end{pmatrix} \qquad \overrightarrow{(U \cdot D)} = \begin{pmatrix} 21756 \\ 5890 \\ 12462 \\ 5814 \\ 1702 \\ 2420 \end{pmatrix}$$

$$\overrightarrow{\sum(T \cdot H)} = 117.759 \qquad \overrightarrow{\sum(U \cdot T)} = 4173.6 \qquad \overrightarrow{\sum(U^2)} = 4460 \qquad \overrightarrow{\sum(U \cdot D)} = 50044$$

$$\overrightarrow{(U \cdot D)} = \begin{pmatrix} 573.3 \\ 152.57 \\ 307.52 \\ 203.3 \\ 253.92 \\ 218.9 \end{pmatrix} \qquad \overrightarrow{(U \cdot B)} = \begin{pmatrix} 25911.48 \\ 1950.73 \\ 22320 \\ 10212.5 \\ 6812.37 \\ 6071.78 \end{pmatrix} \qquad \overrightarrow{(U \cdot C)} = \begin{pmatrix} 8587.32 \\ 1099.34 \\ 3144.95 \\ 717.06 \\ 4232.46 \\ 1716 \end{pmatrix} \qquad \overrightarrow{(U \cdot N)} = \begin{pmatrix} 123.48 \\ 194.18 \\ 252.96 \\ 123.5 \\ 78.2 \\ 57.2 \end{pmatrix}$$

$$\overrightarrow{\sum(U \cdot O)} = 1709.51 \qquad \overrightarrow{\sum(U \cdot B)} = 73278.86 \qquad \overrightarrow{\sum(U \cdot C)} = 19497.13 \qquad \overrightarrow{\sum(U \cdot N)} = 829.52$$

$$\overrightarrow{\left(U^{2}\right)} = \left(\begin{array}{c} \\ \end{array}\right)$$

$$(U \cdot D) = \begin{pmatrix} 21756 \\ 5890 \\ 12462 \\ 5814 \\ 1702 \\ 2420 \end{pmatrix}$$

$$\sum \overrightarrow{(T \cdot H)} = 117.759$$

$$\sum \overrightarrow{(U \cdot T)} = 4173.6$$

$$\sum (U^2) = 4460$$

$$\sum \overrightarrow{(U \cdot D)} = 50044$$

$$(U \cdot O) = \begin{pmatrix} 573.3 \\ 152.57 \\ 307.52 \\ 203.3 \\ 253.92 \\ 218.9 \end{pmatrix}$$

$$\sum (U \cdot O) = 1709.51$$

$$\overrightarrow{(U \cdot B)} = \begin{bmatrix}
1950.73 \\
22320 \\
10212.5 \\
6812.37 \\
6071.78
\end{bmatrix}$$

$$\overrightarrow{(U \cdot B)} = 73278.86$$

$$\overrightarrow{(U \cdot C)} = \begin{pmatrix}
8587.32 \\
1099.34 \\
3144.95 \\
717.06 \\
4232.46 \\
1716
\end{pmatrix}$$

$$\overrightarrow{(U \cdot N)} = \begin{pmatrix}
194.18 \\
252.96 \\
123.5 \\
78.2 \\
57.2
\end{pmatrix}$$

$$\overrightarrow{\sum(U\cdot C)} = 19497.13$$

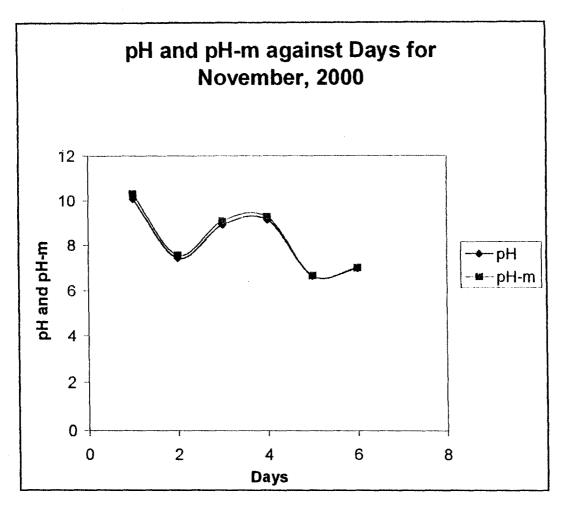
$$\sum \overrightarrow{(U \cdot N)} = 829.52$$

$$(U \cdot P) = \begin{pmatrix} 185.64 \\ 112.86 \\ 122.90.3 \\ 102.22 \\ 22.41 \\ 232.54 \end{pmatrix}$$

$$(U \cdot P) = 705.43$$

$$(D \cdot P) = 705.73$$

Days	рΗ	р	H-m
-	1	10.08	10.308
	2	7.43	7.567
	3	8.91	9.086
	4	9.14	9.271
	5	6.65	6.666
	6	6.98	7.014



#### **AUGUST 2003**

#### **MODELLING**

-11	1	т.,	TDC	DO	DOD.	COD	NO	D ()	ien I
1pm	11	I LU	lino i	וטט	טטמן	COD	INO	IP O	130
11		1			Ĺ				

data :=

	1	2	3	4	5	6	7	8	9	10	11
1	1	8.24	27	15	189	7.28	110.25	600	1.2	5.23	162.5
2	2	6.31	26.6	14.5	234.11	6.7	45.57	260	0.7	1.76	215
3	3	6.77	26.6	14	408.25	6.67	88.2	140	0.5	9.29	130
4	4	7.58	28	12	225.93	7.75	99.96	220	0.5	8.83	87.5
5	5	6.55	27.8	160	228.79	7.41	58.8	380	0.7	7.56	46
6	6	5.83	28	116	216.55	7.76	70.56	319.2	0	6.93	90

$$pH:=data \hspace{0.2cm} \begin{picture}(10,10) \put(0,0){\line(1,0){100}} \put($$

$$D := data$$
 (5)

$$O := data^{-(6)}$$

$$C := data \quad \langle s \rangle \qquad \qquad N := data \quad \langle s \rangle \qquad \qquad P := data \quad \langle to \rangle$$

$$\sum \overrightarrow{(T)^{2}} = 4.485 \times 10^{3} \qquad \sum \overrightarrow{(T \cdot U)} = 9.195 \times 10^{3} \qquad \sum \overrightarrow{(T \cdot D)} = 4.094 \times 10^{4} \qquad \sum \overrightarrow{(T \cdot D)} = 1.192 \times 10^{3}$$

$$\sum \overrightarrow{(T \cdot B)} = 1.294 \times 10^{4} \qquad \sum \overrightarrow{(T \cdot C)} = 5.25 \times 10^{4} \qquad \sum \overrightarrow{(T \cdot N)} = 97.78 \qquad \sum \overrightarrow{(T \cdot P)} = 1.087 \times 10^{3}$$

$$\sum \overrightarrow{(T \cdot S)} = 1.981 \times 10^{4}$$

$$\sum \overrightarrow{(U \cdot T)} = 9.195 \times 10^{3} \qquad \sum \overrightarrow{(U^{2})} = 3.983 \times 10^{4} \qquad \sum \overrightarrow{(U \cdot D)} = 7.638 \times 10^{4} \qquad \sum \overrightarrow{(U \cdot D)} = 2.478 \times 10^{3}$$

$$\sum \overrightarrow{(U \cdot B)} = 2.234 \times 10^{4} \qquad \sum \overrightarrow{(U \cdot C)} = 1.152 \times 10^{5} \qquad \sum \overrightarrow{(U \cdot N)} = 153.15 \qquad \sum \overrightarrow{(U \cdot P)} = 2.353 \times 10^{3}$$

$$\sum \overrightarrow{(U \cdot S)} = 2.623 \times 10^{4}$$

$$\sum \overrightarrow{(D \cdot T)} = 4.094 \times 10^{4} \qquad \sum \overrightarrow{(D \cdot U)} = 7.638 \times 10^{4} \qquad \sum \overrightarrow{(D^{2})} = 4.075 \times 10^{5} \qquad \sum \overrightarrow{(D \cdot C)} = 1.079 \times 10^{4}$$

$$\sum \overrightarrow{(D \cdot B)} = 1.188 \times 10^{5} \qquad \sum \overrightarrow{(D \cdot C)} = 4.372 \times 10^{5} \qquad \sum \overrightarrow{(D \cdot N)} = 867.92 \qquad \sum \overrightarrow{(D \cdot P)} = 1.042 \times 10^{4}$$

$$\sum \overrightarrow{(D \cdot S)} = 1.839 \times 10^{5}$$

$$\sum \overrightarrow{(O \cdot T)} = 1.192 \times 10^3$$
  $\sum \overrightarrow{(O \cdot U)} = 2.478 \times 10^3$   $\sum \overrightarrow{(O \cdot D)} = 1.079 \times 10^4$   $\sum \overrightarrow{(O^2)} = 317.565$ 

$$\sum \overrightarrow{(O \cdot B)} = 3.454 \times 10^{3} \qquad \sum \overrightarrow{(O \cdot C)} = 1.404 \times 10^{4} \qquad \sum \overrightarrow{(O \cdot N)} = 25.823 \qquad \sum \overrightarrow{(O \cdot P)} = 290.06$$

$$\sum \overrightarrow{(O \cdot S)} = 5.208 \times 10^{3}$$

$$\sum \overrightarrow{(O \cdot B)} = 3.454 \times 10^3 \qquad \sum \overrightarrow{(O \cdot C)} = 1.404 \times 10^4 \qquad \sum \overrightarrow{(O \cdot N)} = 25.823 \qquad \sum \overrightarrow{(O \cdot P)} = 290.06$$

$$\sum \overrightarrow{(O \cdot S)} = 5.208 \times 10^3$$

$$\overbrace{\sum(B \cdot T)} = 1.294 \times 10^{4} \qquad \overbrace{\sum(B \cdot U)} = 2.234 \times 10^{4} \qquad \overline{\sum(B \cdot D)} = 1.188 \times 10^{5} \qquad \overline{\sum(B \cdot O)} = 3.454 \times 10^{3}$$

$$\overbrace{\sum(B^{2})} = 4.044 \times 10^{4} \qquad \overline{\sum(B \cdot C)} = 1.572 \times 10^{5} \qquad \overline{\sum(B \cdot N)} = 299.439 \qquad \overline{\sum(B \cdot P)} = 3.292 \times 10^{3}$$

$$\underbrace{\sum(B \cdot S)} = 5.698 \times 10^{4}$$

$$\sum \overrightarrow{(C \cdot T)} = 5.25 \times 10^{4} \qquad \sum \overrightarrow{(C \cdot U)} = 1.152 \times 10^{5} \qquad \sum \overrightarrow{(C \cdot D)} = 4.372 \times 10^{5} \qquad \sum \overrightarrow{(C \cdot D)} = 1.404 \times 10^{4}$$

$$\sum \overrightarrow{(C \cdot B)} = 1.572 \times 10^{5} \qquad \sum \overrightarrow{(C \cdot P)} = 7.419 \times 10^{5} \qquad \sum \overrightarrow{(C \cdot N)} = 1.348 \times 10^{3} \qquad \sum \overrightarrow{(C \cdot P)} = 1.192 \times 10^{4}$$

$$\sum \overrightarrow{(C \cdot S)} = 2.371 \times 10^{5}$$

$$\sum \overrightarrow{(N \cdot T)} = 97.78 \qquad \sum \overrightarrow{(N \cdot U)} = 153.15 \qquad \sum \overrightarrow{(N \cdot D)} = 867.92 \qquad \sum \overrightarrow{(N \cdot O)} = 25.823$$

$$\sum \overrightarrow{(N \cdot B)} = 299.439 \qquad \sum \overrightarrow{(N \cdot C)} = 1.348 \times 10^3 \qquad \sum \overrightarrow{(N^2)} = 2.92 \qquad \sum \overrightarrow{(N \cdot P)} = 21.86$$

$$\sum \overrightarrow{(N \cdot S)} = 486.45$$

$$\sum \overrightarrow{(P \cdot T)} = 1.087 \times 10^{3} \qquad \sum \overrightarrow{(P \cdot U)} = 2.353 \times 10^{3} \qquad \sum \overrightarrow{(P \cdot D)} = 1.042 \times 10^{4} \qquad \sum \overrightarrow{(P \cdot C)} = 290.06$$

$$\sum \overrightarrow{(P \cdot B)} = 3.292 \times 10^{3} \qquad \sum \overrightarrow{(P \cdot C)} = 1.192 \times 10^{4} \qquad \sum \overrightarrow{(P \cdot N)} = 21.86 \qquad \sum \overrightarrow{(P^{2})} = 299.902$$

$$\sum \overrightarrow{(P \cdot S)} = 4.18 \times 10^{3}$$

$$\sum \overrightarrow{(S \cdot T)} = 1.981 \times 10^{4} \qquad \sum \overrightarrow{(S \cdot U)} = 2.623 \times 10^{4} \qquad \sum \overrightarrow{(S \cdot D)} = 1.839 \times 10^{5} \qquad \sum \overrightarrow{(S \cdot O)} = 5.208 \times 10^{3}$$

$$\sum \overrightarrow{(S \cdot B)} = 5.698 \times 10^{4} \qquad \sum \overrightarrow{(S \cdot C)} = 2.371 \times 10^{5} \qquad \sum \overrightarrow{(S \cdot N)} = 486.45 \qquad \sum \overrightarrow{(S \cdot P)} = 4.18 \times 10^{3}$$

$$\sum \overrightarrow{(S^{2})} = 1.074 \times 10^{5}$$

$$H = \begin{pmatrix} 4.485 \times 10^{3} & 9.195 \times 10^{3} & 4.094 \times 10^{4} & 1.192 \times 10^{3} & 1.294 \times 10^{4} & 5.25 \times 10^{4} & 97.78 & 1.087 \times 10^{3} & 1.981 \times 10^{4} \\ 9.195 \times 10^{3} & 3.983 \times 10^{4} & 7.638 \times 10^{4} & 2.478 \times 10^{3} & 2.234 \times 10^{4} & 1.152 \times 10^{5} & 153.15 & 2.353 \times 10^{3} & 2.623 \times 10^{4} \\ 4.094 \times 10^{4} & 7.638 \times 10^{4} & 4.075 \times 10^{5} & 1.079 \times 10^{4} & 1.188 \times 10^{5} & 4.372 \times 10^{5} & 867.92 & 1.042 \times 10^{4} & 1.839 \times 10^{5} \\ 1.192 \times 10^{3} & 2.478 \times 10^{3} & 1.079 \times 10^{4} & 317.565 & 3.454 \times 10^{3} & 1.404 \times 10^{4} & 25.823 & 290.06 & 5.208 \times 10^{3} \\ 1.294 \times 10^{4} & 2.234 \times 10^{4} & 1.188 \times 10^{5} & 3.454 \times 10^{3} & 4.044 \times 10^{4} & 1.572 \times 10^{5} & 299.439 & 3.292 \times 10^{3} & 5.698 \times 10^{4} \\ 5.25 \times 10^{4} & 1.152 \times 10^{5} & 4.372 \times 10^{5} & 1.404 \times 10^{4} & 1.572 \times 10^{5} & 7.419 \times 10^{5} & 1.348 \times 10^{3} & 1.192 \times 10^{4} & 2.371 \times 10^{5} \\ 97.78 & 153.15 & 867.92 & 25.823 & 299.439 & 1.348 \times 10^{3} & 2.92 & 21.86 & 486.45 \\ 1.087 \times 10^{3} & 2.353 \times 10^{3} & 1.042 \times 10^{4} & 290.06 & 3.292 \times 10^{3} & 1.192 \times 10^{4} & 21.86 & 299.902 & 4.18 \times 10^{3} \\ 1.981 \times 10^{4} & 2.623 \times 10^{4} & 1.839 \times 10^{5} & 5.208 \times 10^{3} & 5.698 \times 10^{4} & 2.371 \times 10^{5} & 486.45 & 4.18 \times 10^{3} & 1.074 \times 10^{5} \end{pmatrix}$$

$$\begin{array}{c}
\left(\begin{array}{c}
\sum \overline{(T \cdot pH)} \\
\sum \overline{(U \cdot pH)} \\
\end{array}\right) \\
\sum \overline{(D \cdot pH)} \\
\sum \overline{(O \cdot pH)} \\
\sum \overline{(B \cdot pH)} \\
\sum \overline{(C \cdot pH)} \\
\sum \overline{(N \cdot pH)} \\
\sum \overline{(P \cdot pH)} \\
\sum \overline{(S \cdot pH)}
\end{array}$$

constants = 
$$\begin{pmatrix} 1.128 \times 10^{3} \\ 2.125 \times 10^{3} \\ 1.027 \times 10^{4} \\ 299.941 \\ 3.347 \times 10^{3} \\ 1.355 \times 10^{4} \\ 26.065 \\ 273.945 \\ 5.065 \times 10^{3} \end{pmatrix}$$

c' := lsolve(H, constants)

$$\mathbf{c'} = \begin{pmatrix} 0.465 \\ -0.057 \\ 0.093 \\ 2.915 \\ 0.187 \\ 1.754 \times 10^{-3} \\ -0.737 \\ -5.5 \\ -0.21 \end{pmatrix}$$

 $pH_{\mbox{model}} \coloneqq 0.465 \cdot T - 0.057 \cdot U + 0.093 \cdot D + 2.915 \cdot O + 0.187 \cdot B + 0.001754 \cdot C - 0.737 \cdot N - 5.5 \cdot P - 0.21 \cdot S$ 

# SIMULATION OF MODEL

$$pH_{model} = \begin{pmatrix} 8.393 \\ 6.477 \\ 6.957 \\ 7.709 \\ 6.591 \\ 5.907 \end{pmatrix}$$

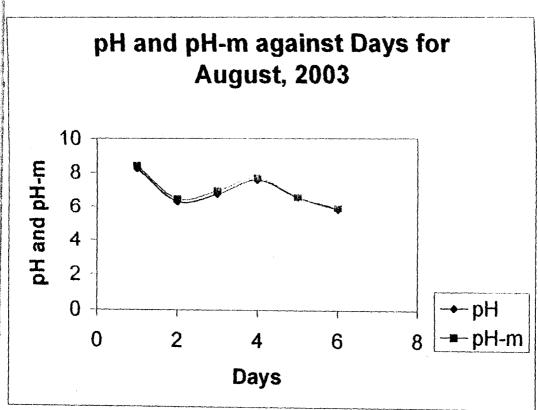
 $error := pII - pII_{model}$ 

error = 
$$\begin{pmatrix} -0.153 \\ -0.167 \\ -0.187 \\ -0.129 \\ -0.041 \\ -0.077 \end{pmatrix}$$

$$\%error := \overline{\left(\frac{error}{pH} + 100\right)}$$

$$\%error = \begin{pmatrix} -1.856 \\ -2.646 \\ -2.759 \\ -1.697 \\ -0.624 \\ -1.323 \end{pmatrix}$$

ys	pН	pH-m			
	1	8.24	8.393		
	2	6.31	6.477		
	3	6.77	6.957		
	4	7.58	7.709		
	5	6.55	6.591		
	6	5.83	5.907		



MAY2004

# PH T Tu TDS DO BOD COD NO PO SO

22 437.71 7.36 29.2 6.8 179.34 360 6.87 42 1.1 2.85 29.1 21 464.57 14.7 46.16 0.4 3.25 165 16 410.85 8.16 199.9 203.08 6.09 29.4 0.5 0.92 200 72.99 80 321.94 267.62 90 27.5 450 95.49 2.6 270 49.65 7.34 98.49 36.5 18.01

pH := data  $\stackrel{\langle 0 \rangle}{}$  T := data  $\stackrel{\langle 1 \rangle}{}$  U := data  $\stackrel{\langle 2 \rangle}{}$  D := data  $\stackrel{\langle 3 \rangle}{}$  O := data  $\stackrel{\langle 4 \rangle}{}$  B := data  $\stackrel{\langle 5 \rangle}{}$  C := data  $\stackrel{\langle 6 \rangle}{}$  N := data  $\stackrel{\langle 7 \rangle}{}$  P := data  $\stackrel{\langle 8 \rangle}{}$  S := data  $\stackrel{\langle 9 \rangle}{}$ 

$$\begin{pmatrix} \sum (\overrightarrow{r}^2) & \sum (\overrightarrow{T} \cdot \overrightarrow{U}) & \sum (\overrightarrow{T} \cdot \overrightarrow{D}) & \sum (\overrightarrow{T} \cdot \overrightarrow{$$

 $\mathsf{M} = \begin{pmatrix} 5 \times 10^3 & 2.42 \times 10^4 & 5.18 \times 10^4 & 8.83 \times 10^3 & 1.72 \times 10^4 & 2.24 \times 10^4 & 1.71 \times 10^2 & 2.12 \times 10^3 & 1.52 \times 10^4 \\ 2.42 \times 10^4 & 2.83 \times 10^5 & 1.08 \times 10^5 & 2.69 \times 10^4 & 5.17 \times 10^4 & 3.17 \times 10^4 & 1.49 \times 10^3 & 2.06 \times 10^4 & 2.15 \times 10^4 \\ 5.18 \times 10^4 & 1.08 \times 10^5 & 6.91 \times 10^5 & 9.67 \times 10^4 & 1.98 \times 10^5 & 3.03 \times 10^5 & 1.33 \times 10^3 & 1.32 \times 10^4 & 2.07 \times 10^5 \\ 8.83 \times 10^3 & 2.69 \times 10^4 & 9.67 \times 10^4 & 7.19 \times 10^4 & 2.34 \times 10^4 & 3.7 \times 10^4 & 1.72 \times 10^2 & 4.04 \times 10^3 & 2.73 \times 10^4 \\ 1.72 \times 10^4 & 5.17 \times 10^4 & 1.98 \times 10^5 & 2.34 \times 10^4 & 8.81 \times 10^4 & 1.18 \times 10^5 & 4.96 \times 10^2 & 5.06 \times 10^3 & 5.9 \times 10^4 \\ 2.24 \times 10^4 & 3.17 \times 10^4 & 3.03 \times 10^5 & 3.7 \times 10^4 & 1.18 \times 10^5 & 1.89 \times 10^5 & 6.09 \times 10^2 & 5.1 \times 10^3 & 7.51 \times 10^4 \\ 1.71 \times 10^2 & 1.49 \times 10^3 & 1.33 \times 10^3 & 1.72 \times 10^2 & 4.96 \times 10^2 & 6.09 \times 10^2 & 9.44 & 1.16 \times 10^2 & 2.8 \times 10^2 \\ 2.12 \times 10^3 & 2.06 \times 10^4 & 1.32 \times 10^4 & 4.04 \times 10^3 & 5.06 \times 10^3 & 5.1 \times 10^3 & 1.16 \times 10^2 & 1.6 \times 10^3 & 2.67 \times 10^3 \\ 1.52 \times 10^4 & 2.15 \times 10^4 & 2.07 \times 10^5 & 2.73 \times 10^4 & 5.9 \times 10^4 & 7.51 \times 10^4 & 2.8 \times 10^2 & 2.67 \times 10^3 & 7.77 \times 10^4 \end{pmatrix}$ 

$$m_{:=} \begin{pmatrix} \sum \overrightarrow{(pH \cdot U)} \\ \sum \overrightarrow{(pH \cdot D)} \\ \sum \overrightarrow{(pH \cdot D)} \\ \sum \overrightarrow{(pH \cdot D)} \\ \sum \overrightarrow{(pH \cdot B)} \\ \sum \overrightarrow{(pH \cdot P)} \\ \sum \overrightarrow{(pH \cdot P)} \\ \sum \overrightarrow{(pH \cdot S)} \end{pmatrix}$$

$$m = \begin{pmatrix} 1.007 \times 10^{3} \\ 5.479 \times 10^{3} \\ 9.783 \times 10^{3} \\ 1.694 \times 10^{3} \\ 3.793 \times 10^{3} \\ 4.924 \times 10^{3} \\ 38.034 \\ 468.603 \\ 2.658 \times 10^{3} \end{pmatrix}$$

$$d' := lsolve(M, m)$$

$$d^{1} = \begin{pmatrix} 0.18 \\ -3.93 \times 10^{-3} \\ 6.797 \times 10^{-3} \\ 8.037 \times 10^{-3} \\ 0.043 \\ -0.025 \\ 2.578 \\ -0.159 \\ -0.033 \end{pmatrix}$$

 $pH_{\ model} := 0.18 \cdot T - 0.00393 \cdot U + 0.006797 \cdot D + 0.008037 \cdot O + 0.043 \cdot B - 0.025 \cdot C + 2.578 \cdot N - 0.159 \cdot P - 0.036 \cdot C + 0.008037 \cdot O + 0.00807 \cdot O + 0.008037 \cdot O + 0.00807 \cdot O + 0.00807 \cdot$ 

$$pH_{model} = \begin{pmatrix} 7.268 \\ 2.916 \\ 6.149 \\ 5.551 \\ 6.609 \\ 6.492 \end{pmatrix}$$

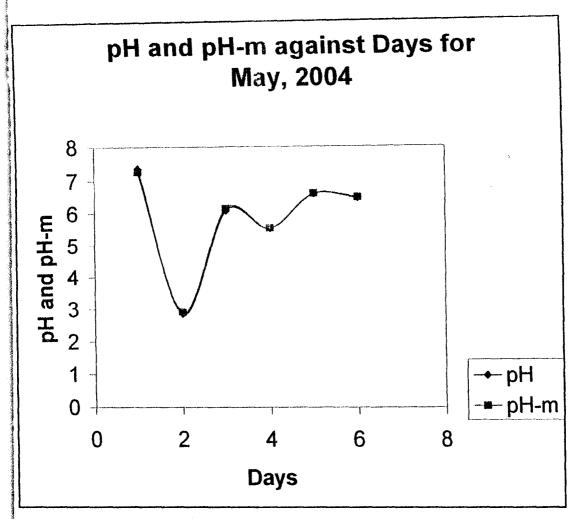
error :=  $pH - pH_{model}$ 

error = 
$$\begin{pmatrix} 0.092 \\ -0.066 \\ -0.059 \\ -0.011 \\ -8.977 \times 10^{-3} \\ -0.022 \end{pmatrix}$$

$$\%error := \left(\frac{error}{pH} \cdot 100\right)$$

$$\%error = \begin{pmatrix}
1.245 \\
-2.321 \\
-0.963 \\
-0.203 \\
-0.136 \\
-0.333
\end{pmatrix}$$

Days	pН	pŀ	<del>l</del> -m
	1	7.36	7.268
	2	2.85	2.916
	3	6.09	6.149
	4	5.54	5.551
1	5	6.6	6.609
and declarate	6	6.47	6.492



# 4.5 DISCUSSION OF RESULTS

The results obtained for the modeled pH of the three months showed that the values were very close to the experimental values. The percentage error for November 2000 ranged from -2.25% to -0.238%, for August 2003 the percentage error ranged from -2.759% to -0.624% also May 2004 have percentage error range of -2.321% to 1.2455.

pH which is the dependent variable depends on certain parameters such as temperature, total dissolved solids, biochemical oxygen demand, chemical oxygen demand, dissolved oxygen, turbidity, Nitrate, Sulphate and Phosphate compounds. These parameters affect the pH of the liquid effluent either directly or indirectly.

Considering the graphs of the three months, it was observed that the curves for the experimental pH and modeled pH overlapped due to the closeness of their values. Take for instance the experimental pH values obtained for November 2000 were 10.08, 7.43, 8.91, 9.14, 6.65, 6.98 with the corresponding modeled pH as 10.308, 7.567, 9.086, 9.271, 6.666, 7.014 respectively. For August 2003, the pH values obtained were 8.24, 6.31, 6.77, 7.58, 6.55 and 5.83 with the corresponding modeled pH as 8.393, 6.477, 6.957, 7.709, 6.591 and 5.907 respectively. The experimental pH values obtained for May 2004 were 7.36, 2.85, 6.09, 5.54, 6.60 and 6.47 with the corresponding modeled pH as 7.268, 2.916, 6.149, 5.551, 6.609 and 6.492 respectively.

The two graphs for November 2000 and August 2003 showed the same pattern of curve which was as a result of similar variation in their pH values. The liquid effluents discharged were either in acidic or basic medium. In case of May 2004,

the liquid effluent was mainly in acidic medium because the values were below 7.0 on the pH scale.

It can be said that pollutants presents in water seriously affect its pH.

Water being an effective solvent can easily be ionized by another compound thereby replacing its ions with other ions causing an increase or decrease in the concentration of hydrogen ions present. Example of such pollutants include Sulphide Phosphate, Nitrate compounds among others.

### **CHAPTER FIVE**

### 5.0 CONCLUSION

pH, which is a term indicating the hydrogen ion concentration of a solution either in acidic or basic medium. It depends upon certain parameters such as temperature, dissolved oxygen, biochemical oxygen demand, pollutants (like Nitrate, Phosphate, Sulphide). These parameters either increase or decrease the pH level of the liquid effluent

The modeled pH equations for the three months were given below

- i. November 2000
  - pHm: = 0.329 . T 0.241 . U+ 0.014 . D + 0.423 . O-0.0011 . B + 0.001.4 . C 0.592 . N 0.00439 . P + 1.421 . H
- ii. August 2003

pHm: = 
$$0.465 \cdot T - 0.057 \cdot U + 0.093 \cdot D + 2.915 \cdot O + 0.187 \cdot B + 0.001754$$
  
.C -  $0.737.N - 5.5 \cdot P - 0.21 \cdot S$ 

iii. May 2004

Comparing the coefficients of the three equations it was observed that the temperature (T), total dissolved solids (D), dissolved oxygen (O) all had positive values, Phosphate (P) has negative value while those of turbidity (U), biochemical oxygen demand (B), chemical oxygen demand (C) and Nitrate (N) changed.

# 5.1 RECOMMENDATION

Facilities for determination of metallic pollutants in the liquid effluent should be provided.

pH of the liquid effluent should be checked before being discharged into the river.

The standard pH (5.6) value for the Industrial liquid effluent should not be neglected

(F.E.P.A).

More treatment procedures should be carried out because most of the pH values were either above or below the standard value stipulated as a result of certain parameters not determined due to faulty equipment and lamp failure.

Government should provide proper funding for the environmental protection agencies to ensure effective implementation of the pre-sent sewage policy.

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