

TREATMENT AND DISPOSAL OF SPENT CAUSTIC AT TEMA OIL REFINERY (TOR)

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Treatment and Disposal of Spent Caustic at TOR

DECLARATION

I hereby declare that this thesis is the result of my own original work undertaken under the supervision of undersigned, that all works consulted have been referenced and that no part of this thesis has been presented for another degree in this University or elsewhere.

CERTIFICATION

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DEDICATION

I dedicate this work to my family especially Joel Ketu, my father and Gladys Ketu Offei, my mother and finally my lovely wife Abigail Aidoo Ketu.

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ABSTRACT

This research was undertaken to address the issues associated with the treatment options ahead of disposal of spent caustic soda from the Tema Oil Refinery (TOR) in Ghana. The specific objectives were to study the usage of caustic soda in the plant of TOR, analyze the nature and form of the residues and designing a treatment method for treating the spent caustic soda.

Sampling and laboratory analyses were carried out at TOR. Composite samples of spent caustic were analyzed for a period of two months and compared with EPA Ghana sector specific effluent quality guidelines for discharge into natural water bodies for oil and gas exploration, production and refining. Parameters analyzed for included pH, Biochemical Oxygen Demand (BOD₅), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Total Suspended Solids (TSS), and concentrations of hydrogen sulphide (H₂S), mercaptan (RSH) and phenol in both influents and effluents. The study revealed that, the measured effluent parameters exceeded the EPA (Ghana) guideline indicating that the plant's current state of treatment for disposal of spent caustic is not adequate. Acid neutralization and Wet Air Oxidation were used to treat the spent caustic. The parameters showed high removal efficiency between 82% and 99%. It is therefore recommended that the spent caustic be neutralized and subjected to wet air oxidation (WAO) to improve on the final effluent wastewater quality. Also desludging of the spent caustic tank must be done as soon as possible in order to improve on the quality of the final effluent that is discharged into the environment.

Table of Contents

DECLARATION.....	i
CERTIFICATION.....	i
DEDICATION.....	ii
ABSTRACT.....	iii
Table of Contents.....	iv
List of Figures.....	ix
List of Tables.....	xi
List of Abbreviations and Acronyms.....	xii
ACKNOWLEDGEMENT.....	xiv
CHAPTER ONE.....	1
1.0 INTRODUCTION.....	1
1.1 BACKGROUND.....	1
1.2 PROBLEM STATEMENT.....	3
1.3 JUSTIFICATION.....	4
1.4 HYPOTHESIS.....	4
1.5 STUDY OBJECTIVE.....	4
1.6 SPECIFIC OBJECTIVES.....	5
CHAPTER TWO.....	6
2.0 LITERATURE REVIEW.....	6
2.1 INTRODUCTION.....	6
2.2 DEFINITION OF SPENT CAUSTIC.....	7
2.3 CAUSTIC PROCESSES.....	7
2.3.1 Dualayer Distillate Process.....	8
2.3.2 Dualayer Gasoline Process.....	8
2.3.3 Electrolytic Mercaptans Process.....	8
2.3.4 Ferrocyanide Process.....	9

Treatment and Disposal of Spent Caustic at TOR

2.3.5 Lye Treatment.....	9
2.3.6 Mercapsol Process	9
2.3.7 Polysulphide Treatment.....	9
2.3.8 Sodasol Process	10
2.3.9 Solutizer Process.....	10
2.3.10 Steam Regenerative Caustic Treatment.....	10
2.3.11 Unisol Process	10
2.4 CLASSIFICATION OF SPENT CAUSTICS.....	11
2.4.1 Sulphidic spent caustic	11
2.4.2 Cresylic spent caustic	11
2.4.3 Naphthenic spent caustic	12
2.5 SOME PROPERTIES OF SPENT CAUSTICS	12
2.5.1 pH	12
2.5.2 Colour	13
2.5.3 Sulphur Compounds	13
2.5.4 Chemical Oxygen Demand (COD).....	13
2.5.5 Biochemical Oxygen Demand (BOD ₅)	14
2.5.6 Phenol	14
2.6 TREATMENT METHODS	14
2.6.1 Wet Air Oxidation (WAO).....	14
2.6.1.1 Wet Oxidation Temperature and Application Spectrum	15
2.6.2 Acid Neutralization.....	16
2.6.3 The Use of Fenton's Reagent	17
2.7 HANDLING OF SPENT CAUSTIC	17
2.8 EFFECTS OF SPENT CAUSTICS	18
2.8.1 Health.....	18
2.8.2 Environmental and Industrial effects.....	19

Treatment and Disposal of Spent Caustic at TOR

CHAPTER THREE	21
3.0 RESEARCH METHODOLOGY	21
3.1 DESCRIPTION OF THE STUDY SITE	21
3.1.1 Site and External Neighbourhood of Tema Oil Refinery	22
3.2 EXPERIMENTAL PROCEDURE	22
3.2.1 Acid neutralization	22
3.2.2 Wet Air Oxidation	22
3.3 METHODOLOGY	23
3.3.1 Desk Study.....	23
3.3.2 Data Collection	23
3.3.2.1 Interviews.....	23
3.3.2.2 Sampling	23
3.3.3 Analysis of Samples	24
3.3.3.1 pH.....	24
3.3.3.2 Phenols.....	24
3.3.3.3 Hydrogen Sulphide / Mercaptans (H ₂ S / RSH).....	24
3.3.3.4 Biochemical Oxygen Demand (BOD ₅).....	24
3.3.3.5 Chemical Oxygen Demand (COD).....	25
3.3.3.6 Total Dissolved Solids (TDS).....	25
3.3.3.7 Total Suspended Solids (TSS)	25
CHAPTER FOUR.....	26
4.0 RESULTS AND DISCUSSION	26
4.1 CHARACTERISTICS OF WASTEWATER	26
4.1.1 pH	27
4.1.2 Organic Matter.....	27
4.1.2.1 Biochemical Oxygen Demand (BOD ₅).....	27
4.1.2.2 Chemical Oxygen Demand (COD).....	28

Treatment and Disposal of Spent Caustic at TOR

4.1.3 Total Suspended Solids (TSS).....	29
4.1.4 Phenol	30
4.1.5 Total Dissolved Solids (TDS).....	31
4.1.7 Mercaptan (RSH).....	32
4.1.6 Hydrogen Sulphide (H ₂ S).....	32
4.2 CORRELATION BETWEEN PARAMETERS	33
4.2.1 Chemical Oxygen Demand (COD) and Biochemical Oxygen of Demand (BOD ₅)	33
4.2.2 Chemical Oxygen Demand (COD) and pH	34
4.2.3 Phenol and Chemical Oxygen Demand (COD).....	35
4.2.4 Total Dissolved Solids (TDS) and Chemical Oxygen Demand (COD)	35
4.2.5 Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD)	36
4.2.6 Mercaptans (RSH) and Chemical Oxygen Demand (COD).....	36
4.2.7 Hydrogen Sulphide (H ₂ S) and Chemical Oxygen Demand (COD)	37
4.2.8 Biochemical Oxygen Demand (BOD ₅) and pH.....	38
4.2.9 Total Dissolved Solids (TDS) and Biochemical Oxygen Demand (BOD ₅).....	38
4.2.11 Hydrogen Sulphide (H ₂ S) and Biochemical Oxygen Demand (BOD ₅)	39
4.2.12 Phenol and Biochemical Oxygen Demand (BOD ₅)	40
4.2.13 Mercaptan (RSH) and Biochemical Oxygen Demand (BOD ₅).....	41
4.2.14 Total Dissolved Solids (TDS) and pH.....	41
4.2.15 Total Suspended Solids (TSS) and pH	42
4.2.16 Phenol and pH	42
4.2.17 Hydrogen Sulphide (H ₂ S) and pH	43
4.2.18 Mercaptan (RSH) and pH	43
CHAPTER FIVE	45
5.0 CONCLUSION AND RECOMMENDATION	45
5.1 CONCLUSION	45

Treatment and Disposal of Spent Caustic at TOR

5.2 RECOMMENDATIONS	46
REFERENCES.....	47
APPENDICES	50
APPENDIX A – DETAILED LABORATORY RESULTS.....	51
APPENDIX B - ENVIRONMENTAL GUIDELINES FOR INDUSTRY IN GHANA.	57
PARAMETER.....	57
APPENDIX C - PUBLICATION	58
BENCH-SCALE TREATMENT OF SPENT CAUSTIC SOLUTION FROM OIL	
REFINERY – A Case Study at Tema Oil Refinery in Ghana.....	58

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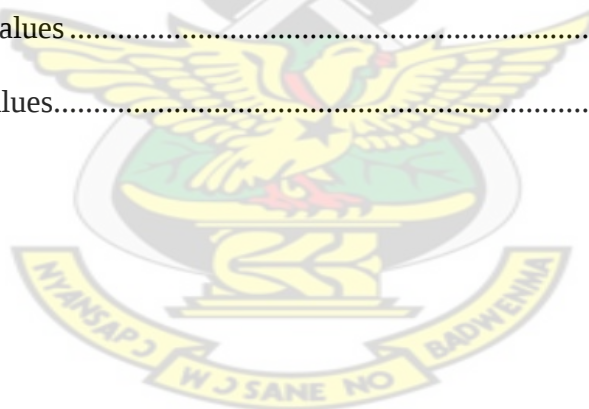
Treatment and Disposal of Spent Caustic at TOR

List of Figures

Figure 2.1: Pictures of Effects of Spent Caustic dumped in Abidjan	19
Figure 2.2: Dilution of a dead stream as a result of spent caustic	20
Figure 3.1: Site Plan of Tema Oil Refinery (TOR) (Code 103 is Sampling point and Code 12 is Quality Control laboratory)	21
Figure 4.1: Plot of pH values and EPA (Ghana) guideline	27
Figure 4.2: Plot of BOD ₅ values and EPA (Ghana) guideline	28
Figure 4.3: Plot of COD values and EPA (Ghana) guideline	29
Figure 4.4: Plot of TSS values and EPA (Ghana) guideline	30
Figure 4.5: Profile of phenol values and EPA (Ghana) guideline	31
Figure 4.6: plot of TDS values and EPA (Ghana) guideline	31
Figure 4.7: Profile RSH values	32
Figure 4.8: Plot of H ₂ S values	33
Figure 4.9: Plot of COD versus BOD ₅	34
Figure 4.10: Plot of COD versus pH	34
Figure 4.11: Profile of phenol versus COD	35
Figure 4.12: Plot of TDS versus COD	36
Figure 4.13: Plot of TSS versus COD	36
Figure 4.14: Plot of RSH versus COD	37
Figure 4.15: Plot of H ₂ S versus COD	37
Figure 4.16: Profile of BOD ₅ versus pH	38
Figure 4.17: Plot of TDS versus BOD ₅	38
Figure 4.18: Plot of TSS versus BOD ₅	39
Figure 4.19: Plot of H ₂ S versus BOD ₅	40
Figure 4.20: Plot of Phenol versus BOD ₅	40

Treatment and Disposal of Spent Caustic at TOR

Figure 4.21: Plot of RSH versus BOD ₅	41
Figure 4.22: Plot of TDS versus pH.....	42
Figure 4.23: Plot of TSS versus pH	42
Figure 4.24: Plot of Phenol versus pH	43
Figure 4.25: Plot of H ₂ S versus pH.....	43
Figure 4.26: Profile of RSH versus pH.....	44
Figure 1: Plot of pH values and EPA (Ghana) guideline	64
Figure 2: Plot of BOD ₅ values and EPA (Ghana) guideline	65
Figure 3: Plot of COD values and EPA (Ghana) guideline	66
Figure 4: Plot of TSS values and EPA (Ghana) guideline.....	66
Figure 5: Profile of Phenol values and EPA (Ghana) guideline	67
Figure 6: Plot of TDS values and EPA (Ghana) guideline	67
Figure 7: Profile RSH values	68
Figure 8: Plot of H ₂ S values.....	68



List of Tables

Table 1.1: Prevailing spent caustic data at TOR versus EPA permissible levels.	3
Table 4.1: Spent Caustic Characteristics.	26



List of Abbreviations and Acronyms

API	American Petroleum Institute
ASTM	America Society for Testing and Materials
ATK	Aviation Turbine Kerosene
BOD ₅	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
CNS	Central Nervous System
EPA	Environmental Protection Agency
EU	European Union
FE	Final Effluent
GHACEM	Ghana Cement Works
H ₂ S	Hydrogen Sulphide
HS	Hydrosulphides
KNUST	Kwame Nkrumah University of Science and Technology
LPG	Liquefied Petroleum Gas
NSC	Neutralized Spent Caustic
RFCC	Residual Fluid Catalytic Cracking
RSH	Mercaptans
SRB	Sulphur Reducing Bacteria
TDS	Total Dissolved Solids
TOC	Total Organic Compounds
TOR	Tema Oil Refinery
TSS	Total Suspended Solids
UOP	Universal Oil Product
USC	Untreated Spent Caustic
VALCO	Volta Aluminum Company
VRA	Volta River Authority

Treatment and Disposal of Spent Caustic at TOR

WAO	Wet Air Oxidation
WWT	Waste Water Treatment

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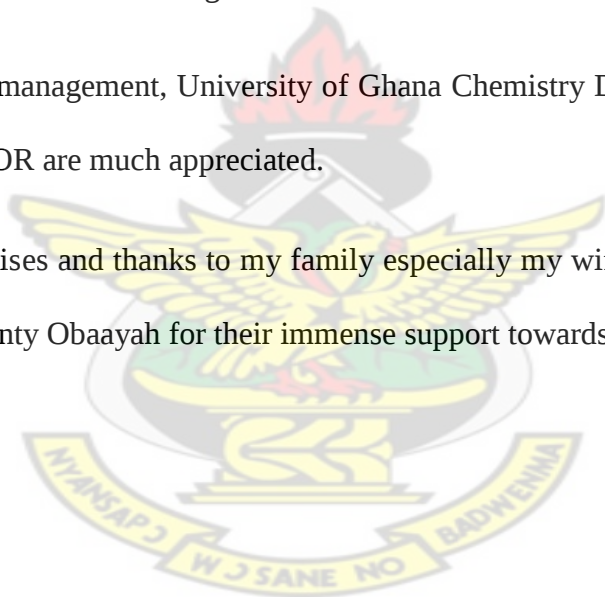
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CHAPTER ONE

1.0 INTRODUCTION

1.1 BACKGROUND

Large scale production of different kinds of chemicals and energy and other developmental activities like agriculture, urbanization and health care have led to the release of huge quantities of wastes into the environment in the form of solid, liquid and gases. A large amount of these wastes is potentially hazardous to the environment and are extremely dangerous to the living organisms including human beings.

“Waste treatment is one of the greatest challenges facing humankind in modern times in spite of the numerous technological achievements that have been well documented. Technology alone has not been able to effectively control waste generated in communities worldwide. Rather, it appears that new technologies bring new types of waste into the environment to add to the complex accumulation puzzle” (Kwarteng, 2001).

It is no secret that waste treatment has been an issue for many hundreds, if not thousands of years. The term ‘out of sight’ might well have summarised waste disposal practices even up to the first few decades of this century. According to Thuy (1998), for the past 53 years, waste has not only progressed to the ‘problem’ stage, it has in many instances become a key factor to investment and development. This has put a lot of pressure on organizations and institutions to conform to the international and local waste treatment standards to enhance their organizational image and improve their market value.

Sodium hydroxide (caustic) scrubbing solutions are commonly used in petrochemical and petroleum refineries for the removal of acid constituents such as hydrogen sulphide (H₂S),

Treatment and Disposal of Spent Caustic at TOR

cresylic acids, mercaptans and naphthenic acids from the refined product streams. When the sodium hydroxide is used in the plant to remove hydrogen sulphide (H_2S), mercaptans, cresylic etc, the resulting waste is called spent caustic soda. Once spent, the caustic solutions can be a challenge to handle and dispose of (Kumfer, Chad and Clay, 2010). Spent caustic typically have a pH greater than 12, sulphide concentrations exceeding 2–3 wt%, and about 80% of residual alkalinity. Depending on the source, spent caustics might contain, for example, mercaptans, H_2S , thiols, phenols, and amines (Kolhatkar and Sublette, 1996).

These constituents in the spent caustic for example phenols are hazardous, H_2S odorous, and / or corrosive. These can cause destruction to ecosystem, bring about diseases and even death.

In Ivory Coast, about 500 metric tonnes of liquid spent caustic were illegally dumped in the Abidjan causing deaths and injuries to local residents. ten people lost their lives, 9,000 people were injured and about 40,000 people reported for medical help after the dumping of untreated spent caustic in various sites in the city of Abidjan. About 197 million dollars have been spent on remediation and claims since the incident began in 2006 (Texas technology, 2006). Spent caustic streams may also have other characteristics that can create issues with conventional biological processes such as noxious odours, pH swings, foaming, or poor settling of biological solids. Effluent requirements may be difficult to achieve because some spent caustic contaminants are not readily biodegradable (Kumfer, Chad and Clay 2010).

The three most common methods for treating spent caustic solutions are wet air oxidation (WAO) and acid neutralization, both followed by biological treatment. In order to treat a spent caustic biologically without pretreatment, spent caustic must be neutralized to a pH range of approximately 6-9. At this pH, many of the constituents present in the spent caustic may be liberated as potentially toxic gases such as hydrogen sulphide and mercaptans. Other constituents such as naphthenic acid have the potential to form a non-water soluble oil layer

Treatment and Disposal of Spent Caustic at TOR

upon neutralization and have been reported to cause foaming issues. In addition, phenols and cresols present as cresylic acids may cause inhibition of efficiency of biological treatment as well as foaming and settling issues (Suarez, 1996). The urgent need to save the environment and lives from destruction necessitate the need to treat any waste that goes to the environment. Many refineries in the world treat or recycle their spent caustic before discharging into the environment. Neutralization has been used to treat spent caustic. This process has not been effective since it could only reduce pH but not reduce or eliminate the other constituents.

Table 1.1 Prevailing spent caustic data at TOR versus EPA permissible levels.

Parameter (mg/l)	Ghana EPA permissible level	TOR values
pH	6-9	14
BOD ₅	50	>50
COD	250	>250
Phenols	0.5	>0.5
Sulphides	1.0	>1.0

Source: Environmental Services Department of TOR, 2012.

After the caustic has been used to remove H₂S, mercaptans etc at the gasoline- LPG merox unit at TOR, nothing is done about it and it is disposed off into a nearby stream which finally ends up in the Chemu Lagoon.

The effluent (spent caustic) causes destruction to the ecosystem and hinders the operation of the Waste Water Treatment (WWT) unit of the refinery (part of the problem). The odourous nature of the spent caustic in the refinery has adverse impact on human lives.

1.2 PROBLEM STATEMENT

Tema Oil Refinery (TOR) produces spent caustic as one of its effluents since its inception. Caustic soda is purposely used in the refining of crude to remove H₂S from the crude. This is introduced at the Merox stage specifically at LPG-gasoline sweetening stage. Conventional disposal methods of dumping in a deep well or the ocean have become environmentally

Treatment and Disposal of Spent Caustic at TOR

unacceptable (Grover and Gomaa, 1993). At Tema Oil Refinery, spent caustic is allowed to go to a storage tank for about three days and later disposed off. Spent caustic at TOR has high pH of about 14, phenol greater than 2, Chemical Oxygen Demand (COD) greater than 250 ppm, Biological Oxygen Demand (BOD₅) greater than 50 ppm and sulphide greater than 1.5 ppm. All these parameters exceed the EPA Ghana permissible levels. This poses great threat to flora and fauna.

1.3 JUSTIFICATION

Treating spent caustic will not only help to safeguard the environment, but will also help the country to forestall unseen future situations like disease outbreak. It will ensure that the corporate responsibility of TOR is adhered to. Corrosion of downstream units will be minimized. Treating spent caustic will ensure that the biological treatment unit of the waste water treatment unit is workable. Treating spent caustic will reduce the insurance premium TOR pays and enhance the process of attaining ISO 14001 by Environmental Services Department and ISO 17025 by Quality Control Department.

1.4 HYPOTHESIS

Spent caustic from petrochemical industries are hazardous to the environment and human life. This spent caustic from TOR can be treated to acceptable standard using neutralization and wet air oxidation to render it harmless to lives and the environment.

1.5 STUDY OBJECTIVE

The main objective is to examine spent caustic at Tema Oil Refinery (TOR) and finding a treatment method before its disposal.

1.6 SPECIFIC OBJECTIVES

- Studying the usage of caustic soda in the plant.
- Analyzing the nature and form of the residues.
- Designing a treatment method for treating the spent caustic soda. Neutralization and Wet Air Oxidation (WAO) would be tried as options ahead of disposal into the environment.



CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

Crude oils are primarily complex mixtures of hydrocarbons ranging from dissolved gases to compounds with small amount of oxygen, nitrogen, sulphur and traces of metals (e.g. vanadium, nickel, iron etc). Crude oil from different sources demonstrates variation in physical and chemical properties (e.g. colour, odour, viscosity etc). These crude oils are refined by the refineries to get their various petroleum products.

A petroleum refinery is an industrial process plant that refines crude oil to different useful petroleum products. It is basically a series of different physical and chemical processes that aim to change the physical and chemical properties of crude oil to make useful products like petrol, diesel, liquefied petroleum gas (LPG), fuel oil, aviation turbine kerosene (ATK) and lubricating oil etc. Due to desired quality of products and environmental regulations different treatment methods are used to get the required specifications. Hydrogen sulphide (H_2S) is removed from the products as it is a very poisonous and toxic gas with rotten egg smell and cannot be left to the environment. In the petroleum industry it is common practice to use caustic solution for treatment of lighter hydrocarbons to remove H_2S (Dando and Martin, 2003). Similarly the LPG stream is treated with caustic solution to remove mercaptans and traces of H_2S but before that amine scrubbing of this stream is done to remove mercaptans (the sulphur containing organic compounds) and H_2S . The strength of the caustic solution decreases with the passage of time and at a certain limit of concentration the solution is replaced with a fresh solution with higher concentration. Spent caustic solution cannot be easily neutralized in most of biological waste water treatment plants due to very high

Treatment and Disposal of Spent Caustic at TOR

chemical oxygen demand (COD). Different solutions and treatment methods are used and suggested for the neutralization of spent caustic (Waqar Ahmad, 2010).

2.2 DEFINITION OF SPENT CAUSTIC

Diluted caustic (NaOH) solutions are often used in the petrochemical industry for the removal of acidic compounds, e.g. volatile (organic) sulphur compounds from hydrocarbon streams, such as gaseous streams and LPG. The use of caustic leads to the formation of a waste product referred to as spent caustic. These spent caustic solutions originating from oil refineries are characterized by a high pH ($\text{pH} > 12$) and elevated sodium concentrations up to 5–12% by weight (Alnaizy, 2008). Hydrosulphide (HS^-) and sulphide (S^{2-}) typically are the most dominant sulphur compounds found in spent caustics with concentrations that may exceed 2–3 wt% (Conner et al 2000). Depending on the source of crude oil, spent caustics might contain e.g., thiols, phenols, mercaptans and amines (Kolhaltkar and Sublette, 1996).

2.3 CAUSTIC PROCESSES

Treatment of petroleum products by washing with solution of alkali (caustic or lye) is done to improve colour and odour by removing organic acids (naphthenic acids and phenols) and sulphur compounds (mercaptans and hydrogen sulphides). The process consists of mixing water solution of sodium hydroxide or caustic soda with petroleum fractions.

There are many caustic processes which are used to treat petroleum products to generate spent caustic. The processes include the following as described by Speight (1994): dualayer distillate process, dualayer gasoline process, electrolytic mercaptans process, ferrocyanide process, lye treatment, mercapsol process, polysulphide treatment, sodasol process, solutizer process, steam regenerative caustic treatment and unisol process.

Treatment and Disposal of Spent Caustic at TOR

2.3.1 Dualayer Distillate Process

The dualayer distillate process extracts organic acidic substances (including RSH) from cracked or virgin distillate fuels. The dualayer reagent (caustic solution and cresylic acid) is mixed with the distillate at about 55 °C (130 °F) and passed to the settler, where three layers separate with the aid of electrical coagulation. The product is withdrawn from the top layer; the dualayer reagent is withdrawn from the bottom layer, relieved of excess water, fortified with additional caustic and recycled until it is about 65% spent.

2.3.2 Dualayer Gasoline Process

This is a modification of dualayer distillate process in that it is used to extract mercaptans from liquid petroleum gas, gasoline and naphtha using dualayer reagent. Thus gasoline, free of hydrogen sulphide is contacted with dualayer solution at 50 °C (120 °F) in at least two stages, after which the treated gasoline is washed and stored. The treating solution now becomes spent which can be diluted with water (60 to 70% of the solution volume) and stripped of mercaptans, gasoline and excess water, and the correct amount of fresh caustic is added to obtain the regenerated reagent .

2.3.3 Electrolytic Mercaptans Process

This process employs aqueous solution to extract mercaptans from refinery streams and the electrolytic process is used to regenerate the solution. The charge stock is pre-washed to remove hydrogen sulphide and contacted counter currently with treating solution in a mercaptans extraction tower. The treated gasoline is stored; the spent is sent for treatment or regenerated by adding fresh solution and oxygen.

Treatment and Disposal of Spent Caustic at TOR

2.3.4 Ferrocyanide Process

It is a regenerated chemical treatment for removing mercaptans from straight –run naphtha as well as natural and recycle gasoline using caustic sodium ferrocyanide reagent. The spent caustic can now be regenerated and used.

2.3.5 Lye Treatment

Lye treatment is carried out in continuous treaters, which essentially consist of a pipe containing baffles or other mixing devices into which the oil and lye solution are both pumped. The pipe discharges into horizontal tank in which the lye solution and the oil separate. Treated oil is drawn from the near top of the tank; lye solution is withdrawn from the bottom and recirculated to mix with the incoming untreated oil. The lye solution is 65% spent after the reaction with hydrogen sulphide, mercaptans organic acids or mineral acids. It is sent to the treatment unit to be treated for disposal.

2.3.6 Mercapsol Process

This is another regenerative process for extracting mercaptans by means of sodium (or potassium) hydroxide, together with cresols, naphthenic acids and phenol. Gasoline is contacted counter currently with the mercapsol solution and the treated product is removed from the top of the tower. Spent solution is stripped to remove gasoline, and the mercaptans are then removed by steam stripping.

2.3.7 Polysulphide Treatment

This is a non-regenerative chemical treatment used to remove elemental sulphur from refinery liquid or products. This is done by dissolving one pound of sodium sulphide in a gallon of caustic solution to prepare the polysulphide solution to remove elemental sulphur.

Treatment and Disposal of Spent Caustic at TOR

2.3.8 Sodalol Process

In this process, lye solution removes only the lighter or lower boiling mercaptans but various chemicals can be added to the lye solution to increase its ability to dissolve the heavier mercaptans.

In sodasol process, the treating solution is composed of lye and alkyl phenols (acid oils). The process is carried out by pumping a sour stream up a treating tower counter current to a stream of sodasol solution that flows down the tower. As the two mix and pass, the solution removes mercaptans and other impurities such as oxygen compounds (phenols and acids) as well as nitrogen compounds. The treated stream leaves the top of the tower; the spent sodasol solution leaves the bottom of the tower.

2.3.9 Solutizer Process

This is a regenerative process using such materials as potassium isobutyrate and potassium alkyl phenolate in strong aqueous potassium hydroxide to remove mercaptans.

2.3.10 Steam Regenerative Caustic Treatment

It is essentially directed towards the removal of mercaptans from product as light as straight-run gasoline. The caustic is regenerated by steam blowing in a stripping tower. The nature and the concentration of mercaptans to be removed dictate the quantity and temperature of the process. However, the caustic solution gradually deteriorates because of the accumulation of materials like phenol and suspended solids that cannot be removed by stripping.

2.3.11 Unisol Process

The unisol process is a regenerative method for extracting not only mercaptans but also certain nitrogen compounds from sour gasoline or distillate. The gasoline free of hydrogen sulphide is washed counter currently with aqueous caustic-methanol solution at about 40 °C

Treatment and Disposal of Spent Caustic at TOR

(100 °F). The spent caustic is regenerated where methanol, water and mercaptans are removed.

2.4 CLASSIFICATION OF SPENT CAUSTICS

There are three types of refinery spent caustics which are known as Sulphidic, naphthenic, and cresylic spent caustic (Suarez, 1996)

2.4.1 Sulphidic spent caustic

Caustics, primarily sodium hydroxide, are used within the petroleum refineries to treat various petroleum streams containing Sulphidic constituents or organic acids (Carlos and Maugans, 2000). Sulphidic caustic streams are generated when light petroleum fractions are treated with a dilute 10% caustic solution to convert odourous or objectionable chemical constituents to their salt forms, which are then soluble in aqueous solution (EU, 2001). This caustic extraction is done to improve colour, odour, and oxidation stability of the petroleum product (API, 2009).

2.4.2 Cresylic spent caustic

Cresylic spent caustic is one of three spent caustics streams originating in oil refineries (Suarez, 1996). Cresylic spent caustic is generated when scrubbing gasoline is produced by fluidized bed catalytic cracking processes with caustic containing high concentrations of organic compounds including phenols and cresols. This type of spent caustic may also contain sulphides and mercaptans. The phenolic content of cresylic spent caustic can be up to 10-25%, which is high enough to make phenolic recovery a profitable option (API, 2009). The majority of phenols present in refinery spent caustic solutions originate from the processing of heavy cracked naptha streams.

2.4.3 Naphthenic spent caustic

Naphthenic spent caustic is produced from the caustic scrubbing of kerosene and diesel products which contain high concentrations of polycyclic aliphatic organic compounds such as naphthenic acids. Naphthenic acids are also known to foam under low temperature WAO treatment conditions, so higher temperatures are employed to destroy the naphthenic compounds and to control foaming. Nearly all the spent acid generated at refineries is regenerated and recycled (API, 1997). The tar acid extracts from crude oil are generally derived from the treatment of cracked naptha streams with caustic concentrations of 10% or greater (Gallo *et al.*, 1952). Cresylic spent caustic is very similar to naphthenic spent caustic in content of COD and TOC, behaviour, and treatment requirements.

2.5 SOME PROPERTIES OF SPENT CAUSTICS

Properties of spent caustic that would be discussed below include pH, colour, sulphur compounds, Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD₅), and Phenol concentrations.

2.5.1 pH

pH, also a potential of hydrogen is defined as the negative logarithm of hydrogen-ion concentration (Pankratz, 2000). Specifically, pH is the negative logarithm of the molar concentration of hydrogen ions. i.e. $\text{pH} = -\log [\text{H}^+]$. Because pH is measured on a logarithmic scale, an increase of one unit indicates an increase of ten times the amount of hydrogen ions. A pH of 7 is considered to be neutral. Acidity increases as pH values decrease, and alkalinity increases as pH values increase. The pH value of spent caustic is between 13 -14.

2.5.2 Colour

The colour of spent caustic depends on the composition. Sulphidic spent caustic is a reddish liquid with a pungent smell, cresylic / phenolic spent caustic is a brownish liquid with tar like odour and naphthenic spent caustic is a dark brown oily liquid with tar like odour.

2.5.3 Sulphur Compounds

Hydrogen sulphide (H_2S) is a naturally occurring gas contained in many of the world's crude oils. It is also formed in the refining process by the degradation of sulphur-containing compounds in crude at high temperatures (Baker Hughes, 2011).

These are among the most important heteroatomic constituents of petroleum. Sulphur compounds of various types can exist in crude depending upon the geological environment of the crude oil field and also on the basic characteristics of its formation. The quantum of sulphur compounds in crudes can be generalized by the statement that: "the higher the density of the crude oil (or the lower the API gravity of the crude oil) the higher the sulphur content". The total sulphur in the crude can vary from, 0.04% for a light paraffin oil to about 5.0% for a heavy crude oil. The following gives the various types of sulphur compounds possibly found in crudes & distillates; Hydrogen Sulphide, Methyl mercaptans, Phenyl mercaptans, Dimethyl Sulphide, Di-n-butyl sulphide, Dimethyl disulphide, Methyl sulphonic acid, Thiophene, Dimethyl sulphone and Dimethyl sulphoxide.

2.5.4 Chemical Oxygen Demand (COD)

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Because of its unique chemical properties, the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is the specified oxidant, and is reduced to the chromic ion (Cr^{+3}). Both organic and inorganic constituents of a sample are subject to oxidation, but in most cases the organic

Treatment and Disposal of Spent Caustic at TOR

constituent predominates and is of the greater interest. The COD of refinery spent caustic is between 1,000 to 45,000 mg/l.

2.5.5 Biochemical Oxygen Demand (BOD₅)

In any water system, microorganisms will consume any organic & inorganic matter added to it and will produce biomass using oxygen present in the water. The oxygen required for the degradation of the organic matter biologically is called the Biochemical Oxygen Demand (BOD₅).

2.5.6 Phenol

Phenol is an inhibitory and toxic compound present in wastewater from petroleum refining, petrochemical, coke conversion and pharmaceutical plants (Lasllai *et al*, 1989). Although inhibitory and toxic, phenol is also a carbon and energy source for some microorganisms. (Rozich *et al*, 1983)

2.6 TREATMENT METHODS

The three main available treatment methods for spent caustic treatment are; Wet Air Oxidation, acid neutralization and the use of Fenton's reagent

2.6.1 Wet Air Oxidation (WAO)

More than 40 years ago, Zimmermann was seeking for an alternative method to treat special black liquors from paper mills. Because of their very high silica content, the usual evaporation and combustion method (Kraft process) was unsuitable. Zimmermann found he could burn pulpmill liquors and described a method using air at high pressure leading to the combustion of organic compounds dissolved or suspended in liquid water, at relatively low temperatures, as long as oxygen was present. Wet air oxidation was beginning to take off. Zimmermann added that this new method was quite similar to incineration as the organic residues were mainly burned up to carbon dioxide, to nitrogen (ammonia or molecular) and to

Treatment and Disposal of Spent Caustic at TOR

ashes, together with a limited amount of volatile fatty acids (acetic) and traces of carbon monoxide. When the temperature was about 300 °C, the organic matter removal efficiency exceeded 95% and enabled the mineral fraction of the oxidized liquor to be recycled. The basic idea of the process is to enhance contact between molecular oxygen and the organic matter to be oxidized. High temperature conditions convert the organic matter to carbon dioxide and water. The liquid phase is maintained by a high pressure which also increases the concentration of dissolved oxygen and thus the oxidation rate. Typical conditions are 260-320 °C for temperature, 25-175 bars for pressure and one hour for the residence time. WAO is one of the few processes that does not turn pollution from one form to another, but really makes it disappear (Himmelblau, 1960).

WAO is a liquid phase reaction using dissolved oxygen in water to oxidize contaminants. The oxidation reactions are performed at elevated temperatures requiring a pressurized system in order to control evaporation. The WAO technology when utilized for the treatment of spent caustic can be further divided into three categories based upon the temperature that is used to perform the oxidations (Kumfer *et al*, 2010).

- Low temperature WAO – typically performed at 100-200 °C and (25 to 100 psig)
- Mid Temperature WAO - typically performed at 200-260 °C and (300 to 600 psig)
- High Temperature WAO - typically performed at 260-320 °C and (700 to 1100 psig)

2.6.1.1 Wet Oxidation Temperature and Application Spectrum

According to Teletzke (1996), the wet oxidation reactions take place between 100 and 372 °C at elevated pressures to maintain water in the liquid phase. This temperature range can be further subdivided into low (100 - 200 °C), medium (200 - 260 °C), and high temperature (260 - 320 °C) operation. Higher temperature (320 - 372 °C) systems can be designed as well but are rarely used.

Treatment and Disposal of Spent Caustic at TOR

Industrial applications of low temperature oxidation (100-200 °C) include the thermal conditioning of sludge and low strength sulphidic spent caustic treatment. Some sulphidic caustics are also treated in this temperature range. Other industrial wastes potentially suitable for low temperature oxidation include cyanide and phosphorous wastes as well as non-chlorinated pesticides. Medium temperature (200 - 260 °C) oxidation is used for typical ethylene spent caustics and some industrial wastes. Ethylene spent caustics are derived from Sulphidic acid gas washings in the ethylene industry. These wastes are treated in the 200 - 220 °C range. Some other industrial wastes containing phenolic or cresylic compounds can be treated at the high end of this temperature spectrum. High temperature (260 - 320 °C) oxidation is used for refinery spent caustic, sludge destruction, and most WAO treated industrial wastewaters. High temperature systems are usually designed for less than 290 °C operation, which is a transition point for higher strength fabrication conventions. Within the 260 - 280 °C range, refinery spent caustics containing significant concentrations of naphthenic and cresylic acids are treated. Most organic industrial wastes are oxidized in this temperature range as well, including chlorinated pesticides, solvents, pharmaceutical and other organic chemical production wastes. Sludge destruction systems are designed to operate within the higher end of this temperature range (260 - 320 °C) and are employed for complete destruction of municipal, pulp and paper, or other organic sludges. The choice of Wet Air Oxidation is based on the fact that it allows onsite treatment without producing odourous off gas (Maugans and Huaman, 2007).

2.6.2 Acid Neutralization

In the acid neutralization treatment process, the spent caustic wastewater is acidified to release acidic constituents that were captured in the alkaline caustic solution. This results in sulphides and mercaptans being released as acid gases and naphthenic acids to be sprung as an oil layer. One large differentiation between acid neutralization and WAO is that the acid

Treatment and Disposal of Spent Caustic at TOR

constituents in the spent caustic are removed but not destroyed. In some cases this results in additional treatment to be required. In others it allows for the capture and re-use of some of the constituents in the spent caustic.

2.6.3 The Use of Fenton's Reagent

Fenton's reagent ($\text{Fe}^{2+} / \text{H}_2\text{O}_2$) can oxidize refractory pollutants at a low temperature and pressure (Shih-Hsiung and Hung-Shan, 2000). But due to a high COD value of spent caustic, it consumes a large amount of H_2O_2 . Also, because of a high concentration of H_2S (up to 20 g/l), its reaction with ferric ion causes a loss of iron catalyst activity. The spent caustic is first neutralized with sulphuric acid to pH of 5.0. Fenton's reagent is then added to oxidize the solution. As a result, the spent caustic treatment becomes economical and effective.

2.7 HANDLING OF SPENT CAUSTIC

Spent caustic produced in industries is handled in many traditional ways. Spent caustic may be of many types depending upon the industry producing it. Spent caustic is produced at refinery plants, chemical manufacturing plants, LPG plant, Natural gas plant and geothermal energy plants etc. The most common and most dangerous compound in all spent caustics is the hydrogen sulphide which is highly toxic and odorous. (Bouma, 2010) There are many traditional and advanced methods used in the industry to handle spent caustic solution. Some of these are listed below:

- Deep well injections
- Dilution and then treatment at waste water treatment plant
- Incineration
- Oxidation methods like wet air oxidation, catalytic oxidation etc
- Export to pulp and paper mills

Treatment and Disposal of Spent Caustic at TOR

Usually, at oil refining plant there are three types of spent caustics produced i.e. sulphidic, naphthenic and phenolic spent caustics. If sulphidic and naphthenic spent caustics are produced at the refinery then their reuse is recommended by experts for crude oil neutralization. For using this spent caustic as crude oil neutralization there should be a wash water system present to avoid the accumulation of these compounds in the overhead system.

The benefit of using the spent caustic for neutralizing crude oil is that the amount of spent caustic produced at the plant will be decreased resulting in less spent caustic to get rid of. The negative effect of using this spent caustic is that the concentration of sodium is not constant and proper injection amount is difficult to control. So, some experts advice to never use spent caustic for neutralization purposes as it may cause higher concentration of sodium in the products and improper control of chloride content in the overhead (Ahmad, 2010).

2.8 EFFECTS OF SPENT CAUSTICS

Depending upon the types and quantity of products being produced and for easy discussion, effects of spent caustic are categorised as follows:

2.8.1 Health

Sulphides and mercaptans have very strong odours. The odour thresholds for these types of compounds are generally in the order of magnitude of parts per billion. Hydrogen sulphide is especially insidious because it deadens the sense of smell at concentration at low as 30 mg/l. Death can occur within a few breaths at low concentration of 700 mg/l. (Baker Hughes, 2011). Spent caustic can cause severe corrosion to the eyes and this leads to corneal opacity. It may also cause severe irritation, redness and tearing, blurred vision and conjunctivitis and finally blindness. Skin contact can produce inflammation and blistering. This causes severe burns with deep ulcerations. Inhalation of spray or mist of spent caustic may produce severe irritation of the respiratory tract characterized by coughing, choking or shortness of breath.

Treatment and Disposal of Spent Caustic at TOR

Additionally, inhalation of high concentrations may cause central nervous system (CNS) depression and/or chemical pneumonitis. In worst cases, immediate coma and death may occur. It is harmful or fatal when swallowed.



Figure 2.1: Pictures of Effects of Spent Caustic dumped in Abidjan
(Source: Texas Technology Corporation, 2012)

2.8.2 Environmental and Industrial effects

Spent Caustic is expected to be toxic to aquatic organisms in the immediate vicinity of release to a body of water due to an increase in pH. Spent Caustic is not expected to bioconcentrate in fish or other aquatic organisms. If Spent Caustic is released to water or soil, constituents are not likely to volatilize to the atmosphere, but will partition primarily to the sediment or remain in the soil. Fate in the soil and sediment will depend on the amount released and the composition of the receiving medium. Depending on the properties of the soil, some constituents may display high mobility. The lower chain alpha olefins in the floating hydrocarbon layer will rapidly volatilize from water or soil to the atmosphere where they will degrade quickly. The higher chain alpha olefins may partition to the soil and sediment where degradation will occur, but at a slower rate (Phillips, 2010). Spent caustic wastewater can cause issues in biological treatment processes. Phenol in concentrations as low as 400 mg/l have been shown to inhibit the removal of COD, ammonia and phosphorous as well as negatively impact the settling characteristics of the sludge (Hidarinasab *et al*, 2011).



Figure 2.2: Dilution of a dead stream as a result of spent caustic

(Source: Texas Technology Corporation, 2012)





1. *What is the purpose of this study?*

Treatment and Disposal of Spent Caustic at TOR

3.1.1 Site and External Neighbourhood of Tema Oil Refinery

Tema Oil Refinery is located at the Heavy Industrial Area of Tema on the VALCO Road. It is linked to an oil jetty at Tema Harbour by pipelines of various diameters for movement of raw materials and finished products. The land area of the refinery is 440,000 m². The large land area provides opportunity for on-site treatment and disposal of some solid wastes.

Neighbouring companies:

South : TOR Operational Tanker Park/Ferro Fabrik/Massily Ghana Limited
West : Karnebo Textile (Pty) Limited/Galvanised Domestic Products Limited
North : Expom Ghana Limited/Desimone Limited/Cirrus Oil
East : VRA/Sentuo Steel Limited

3.2 EXPERIMENTAL PROCEDURE

3.2.1 Acid neutralization

Acid neutralization testing was performed using concentrated hydrochloric acid to adjust the pH to <9 by the process of titration.

3.2.2 Wet Air Oxidation

Laboratory autoclave was used to perform WAO testing. Spent caustic was placed into an autoclave and charged with compressed air. The volume of air was controlled by pressure valves. The autoclave was held at a temperature of 250 °C for a reaction time of 40 minutes.

3.3 METHODOLOGY

The methodology includes desk study, data collection, interviews, sampling and sample analysis.

3.3.1 Desk Study

Desk study was done by obtaining information from Tema Oil Refinery (TOR), internet and review of journals.

3.3.2 Data Collection

Interviews and composite sampling were the techniques used in obtaining information for the work. Other information was obtained from the plant records at TOR.

3.3.2.1 Interviews

First-hand information of the generation of spent caustic at the plant was solicited from senior supervisor and technicians of Residual Fluid Catalytic Cracking (RFCC) unit. Engineers were interviewed to know current state of the plant, caustic usage, the caustic processes and disposal of spent caustic.

3.3.2.2 Sampling

Determination of sampling methodology was tested using both grab sampling method and composite sampling method in order to test the suitability of each sampling method or otherwise. Composite sampling was preferred over grab sampling in order to ensure homogeneity of samples.

Requisite samples were taken during the second week, third week and the fourth week of January 2012. In all, nine composite samples were taken. Sampling was done in the morning using 500 ml amber bottles. The samples were kept in ice to maintain temperatures below 4⁰ C and were transported to the laboratory for analysis.

3.3.3 Analysis of Samples

Parameters that were analysed for are pH, phenol, RSH/H₂S, BOD₅ COD, TDS and TSS for each sample taken.

3.3.3.1 pH

The pH of the solutions was determined using OAKTON pH meter with the sensitivity level of ± 0.01 . The pH meter was calibrated by using reference solution buffers 7, 8 and 10.

3.3.3.2 Phenols

Phenol concentrations were determined using direct photometric method according to American Society for Testing and Materials (ASTM) D1783 -01. This method is based on the reaction of the steam distillate phenolic compounds with 4-amino-antipyrine to produce yellow coloured complex in the presence of potassium ferricyanide [(K₂Fe(CN)₆] at a pH of 10.0 ± 0.2 . The antipyrine colour formed in an aqueous solution was measured at 510 nm. The concentration of the phenolic compounds in the sample is expressed in terms of mg/l of phenol.

3.3.3.3 Hydrogen Sulphide / Mercaptans (H₂S / RSH)

Sulphur and mercaptan concentrations were determined using the Universal Oil Products (UOP) 163-10 test method. 0.25 ml of the sample (spent caustic) was measured into 25 ml beaker. 100 ml of ammoniacal buffer (NH₄OH/NH₄CL) was added and titrated with 0.01M alcoholic silver nitrate (C₂H₅OH/AgNO₃) using the Metrohm Titroprocessor. The H₂S/RSH concentrations were recorded from the Metrohm Titroprocessor sensor.

3.3.3.4 Biochemical Oxygen Demand (BOD₅)

The Biochemical Oxygen Demand (BOD₅) was determined using the respirometric method according to International Standard Organization (ISO) 5815. 350 ml of the homogenous sample was taken and poured into the incubation bottle. Magnetic stirrer was put into the

Treatment and Disposal of Spent Caustic at TOR

incubation bottle and 3.33 mg of nitrification inhibitor was added to the sample in the BOD₅ bottle. An amount of 2.0 g LiOH was put into the neck of the bottle. The pressure sensor was zeroed. The BOD₅ bottle containing the sample was incubated in the BOD₅ incubator at 20 ±1°C for five days. The BOD₅ value was read from the pressure sensor after the 5 days incubation period.

3.3.3.5 Chemical Oxygen Demand (COD)

The COD was determined using the closed reflux colorimetric method according to American Society for Testing and Materials (ASTM) D1252-06. 0.2 ml of the sample was taken and diluted with 2.5 ml of water. 2 ml of diluted sample was added to the COD digestion reagent and the mixture shaken upside down several times to mix thoroughly. The ampoule was placed in a COD reactor and heated for two hours. After two hours, it was placed in a rack and allowed to cool to room temperature. The spectrophotometer was set to the wavelength of High Range (HR) 435 nm and the sample was placed in the spectrophotometer to measure the COD value.

3.3.3.6 Total Dissolved Solids (TDS)

The Total Dissolved solids (TDS) was determined using the OAKTON TDS meter with sensitivity level of ±10 mg/l by dipping the probe of the meter into the 500 ml sampling bottle containing spent caustic. The meter was calibrated using 1500 mg/l reference solution.

3.3.3.7 Total Suspended Solids (TSS)

TSS was determined using a portable spectrophotometer. The instrument was calibrated by placing a reference solution (demineralised water) inside the spectrophotometer cell and readings were zeroed at a wavelength setting of 630 nm. The sample was then placed in the cell to measure the TSS value.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 CHARACTERISTICS OF WASTEWATER

In order to ascertain the characteristics of spent caustic at TOR, laboratory analyses were carried out for various parameters. Table 4.1 shows the characteristics of samples of untreated spent caustic, neutralised spent caustic, final effluent of the wastewater and EPA (Ghana) sector-specific effluent quality guidelines for discharge into natural water bodies for oil and gas exploration, production and refining. The table also includes the statistical analysis output of the results obtained.

Table 4.1: Spent Caustic Characteristics.

	Untreated Spent Caustic (USC)		Neutralised Spent Caustic (NC)		Final Effluent (FE)		
Parameter	Average Value	% Error	Average Value	% Error	Average Value	% Error	EPA (Ghana) permissible values
pH	14.00	0.00	8.16	7.69	6.88	1.94	6 – 9
COD (mg/l)	3,822.01	3.81	632.18	6.55	203.49	4.47	250
BOD ₅ (mg/l)	1,788.36	5.55	598.75	4.45	38.28	7.01	50
Phenol (mg/l)	2.11	28.57	1.67	20.00	0.01	0.00	0.5
H ₂ S (mg/kg)	2,157.36	7.67	731.95	3.13	250.47	5.38	-
RSH (mg/kg)	368.18	7.36	171.91	8.83	21.13	5.18	-
TDS (mg/l)	15.19	3.69	0.43	12.03	0.04	5.18	50
TSS(mg/l)	39.78	5.13	12.33	5.41	6.62	10.53	50

Treatment and Disposal of Spent Caustic at TOR

4.1.1 pH

All the effluents were alkaline in nature with the pH values ranging from 14 to 6.87. The pH generally decreased after each treatment. The average pH of the untreated spent caustic, neutralised spent caustic and the final effluent are 14, 8.16 and 6.88 respectively. The pH of the neutralized caustic and the final effluents were within the EPA Ghana guideline range of 6 – 9 which indicates that the treatment of the sample has been achieved. The Figure 4.1 below shows the plot of sample pH values and EPA Ghana guideline range.

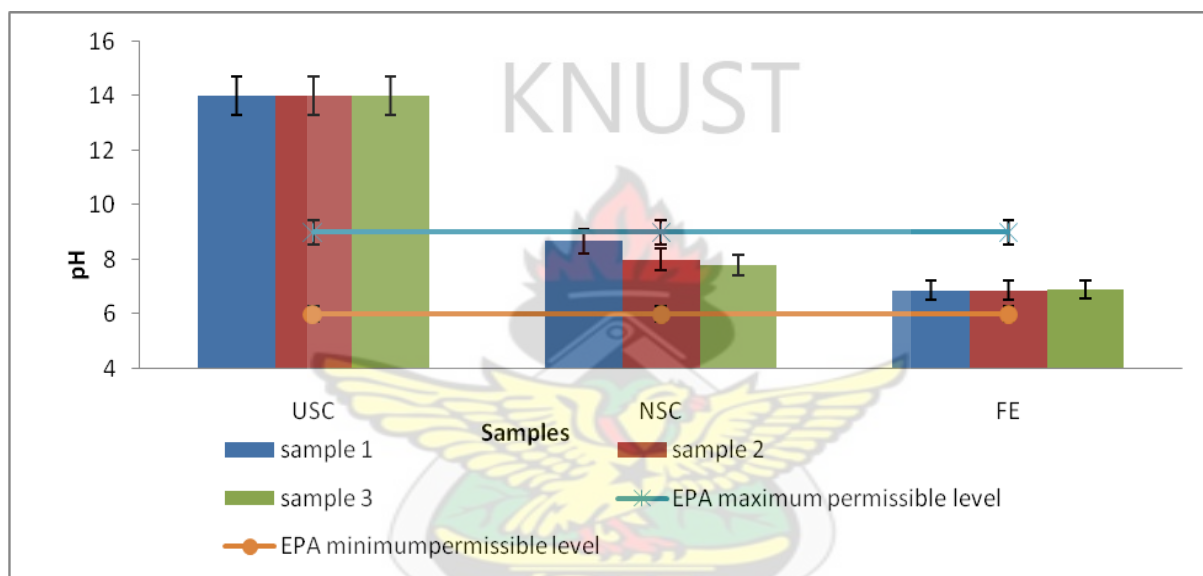


Figure 4.1: Plot of pH values and EPA (Ghana) guideline

4.1.2 Organic Matter

An indication of organic content of the effluent and the receiving water can be accessed from the Biochemical Oxygen Demand (BOD_5) and Chemical Oxygen Demand (COD) levels (Tchobanoglous et al, 2003).

4.1.2.1 Biochemical Oxygen Demand (BOD_5)

The average BOD_5 value of untreated spent caustic, neutralized spent caustic and final effluent were 1788.36 mg/l, 598.75 mg/l and 203.50 mg/l respectively. The average percentage removal of BOD_5 after neutralization is 66.51% while the average percentage

Treatment and Disposal of Spent Caustic at TOR

removal after wet air oxidation (WAO) is 88.62%. The BOD_5 average values of spent caustic and neutralized spent caustic did not meet the EPA Ghana permissible guideline value of 50 mg/l while the average BOD value of the final effluent after WAO was within the EPA Ghana guideline. According to Tchobanoglous et al (2003), the BOD_5 / COD ratio of untreated wastewater range from 0.3 to 0.8. A ratio of 0.5 and above means the wastewater can solely be treated by biological means but any value below 0.3 means the wastewater has some toxic constituents. In the case of this work, the BOD_5 / COD ratio of the final effluent is 0.2 hence the final effluent may contain some traces of toxic substances. Figure 4.2 is the plot of average BOD_5 results of untreated spent caustic, neutralized spent caustic, the final effluent and EPA (Ghana) guideline.

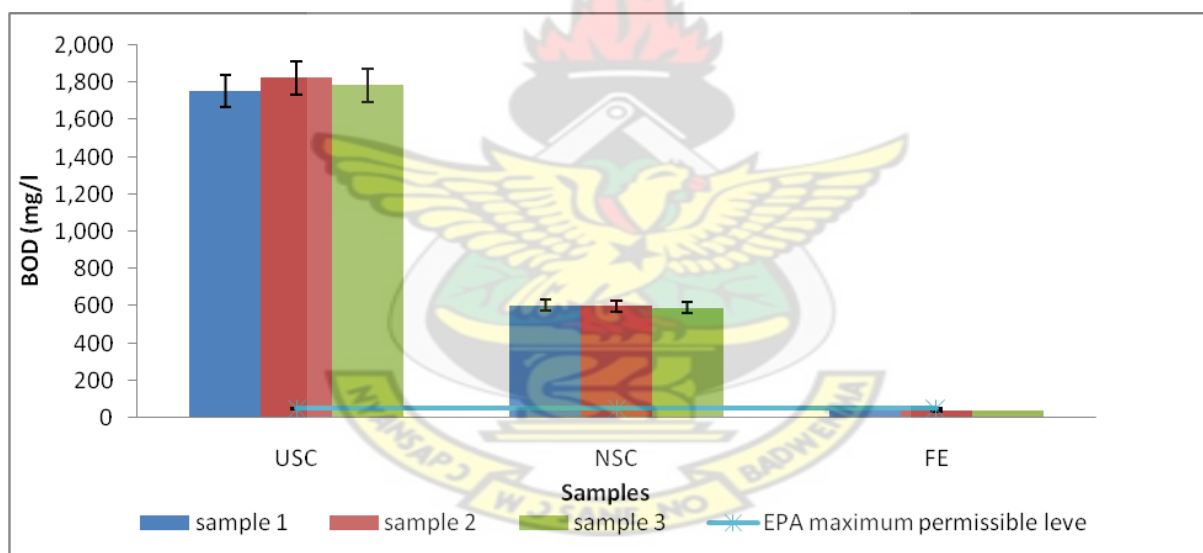


Figure 4.2: Plot of BOD_5 values and EPA (Ghana) guideline

4.1.2.2 Chemical Oxygen Demand (COD)

There was general decrease in COD after neutralization of the spent caustic and further decrease as the neutralized caustic solution was subjected to wet air oxidation. According to Russel (2006), the COD values are higher than the BOD_5 values and this is due to common interference of sulphides, sulphites, thiosulphate and chlorides if present in the solution. The average COD values of the untreated spent caustic, neutralized spent caustic and the final

Treatment and Disposal of Spent Caustic at TOR

effluent were 3822.01 mg/l, 632.18 mg/l and 203.49 mg/l respectively. The average percentage reduction of COD after neutralization was 88.47% and after wet air oxidation is 97.60%. The average COD value of the final effluent was below the EPA Ghana guideline of 250 mg/l but that of the untreated spent caustic and neutralized caustic values were greater than the EPA Ghana guideline. Figure 4.3 below shows the plot of the average COD results of untreated spent caustic, neutralized spent caustic and the final effluent compared with EPA Ghana guideline.

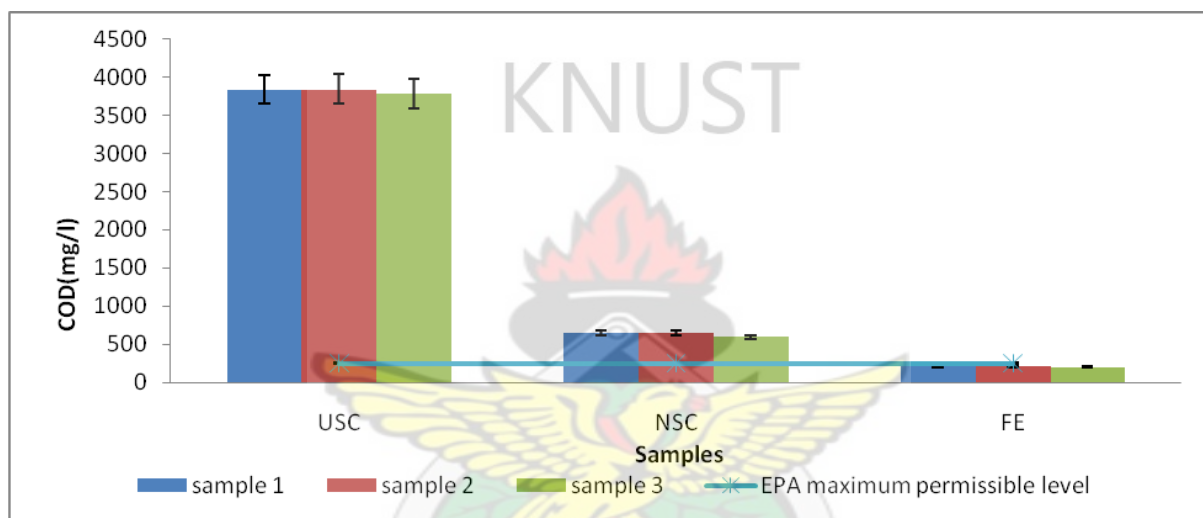


Figure 4.3: Plot of COD values and EPA (Ghana) guideline

4.1.3 Total Suspended Solids (TSS)

The mean TSS value of the untreated spent caustic, neutralized spent caustic and final effluents were 39.78 mg/l, 12.33 mg/l and 6.62 mg/l respectively.

The spent caustic tank has never been desludged and this may have contributed to this increase of TSS value. It was well noted that all the average effluent results complied with the EPA (Ghana) permissible guideline of <50 mg/l. Figure 4.4 is a plot of TSS results obtained from field work compared to EPA (Ghana) guideline.

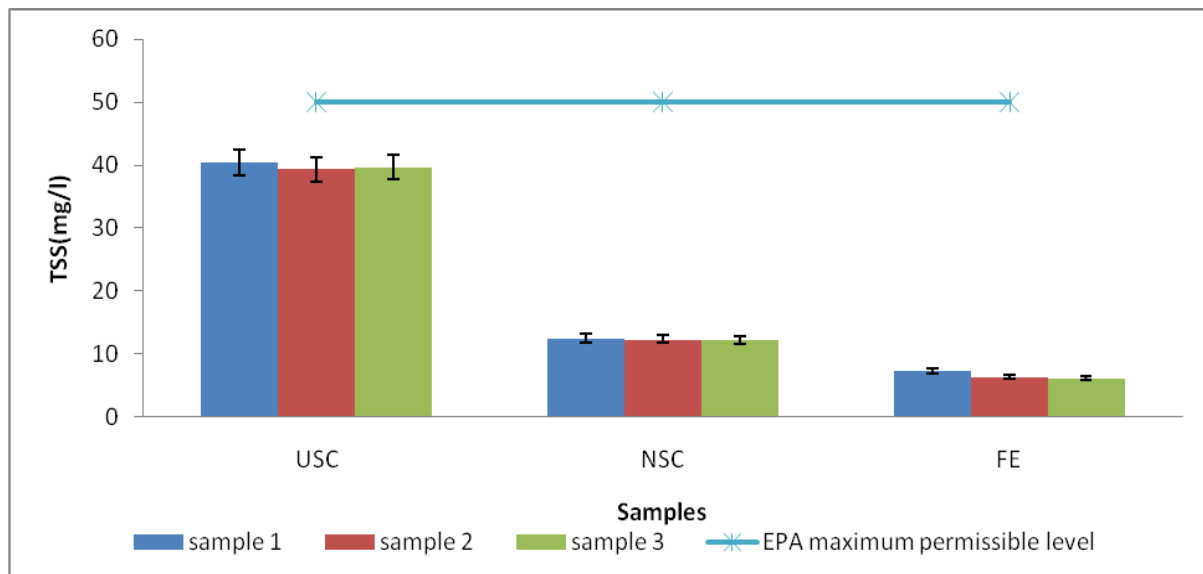


Figure 4.4: Plot of TSS values and EPA (Ghana) guideline

4.1.4 Phenol

There was a general decrease in the phenol concentration after neutralization of the spent caustic but the decrease after wet air oxidation was very drastic. The mean phenol values of untreated spent caustic, neutralized spent caustic and final effluent were 2.11 mg/l, 1.67 mg/l and 0.01 mg/l respectively. 16.65% and 99.52% reduction in concentration were observed after neutralization and wet air oxidation respectively. The concentration of phenol in the final effluent was below the EPA (Ghana) guideline of 0.5 mg/l. Figure 4.5 shows the plotted phenol values from field work and EPA (Ghana) guideline.

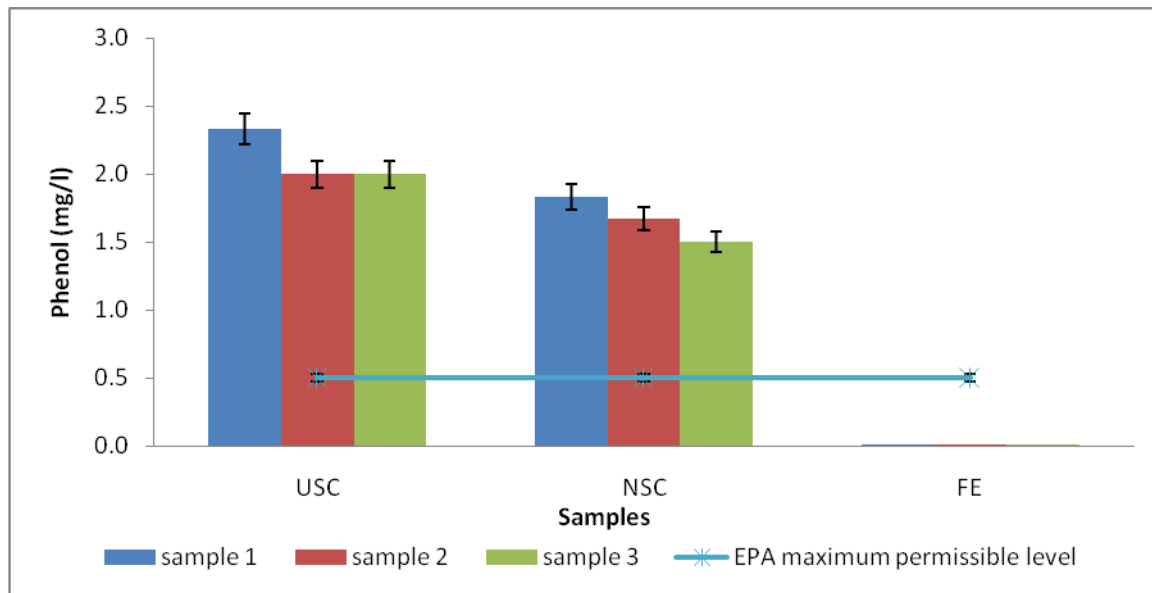


Figure 4.5: Profile of phenol values and EPA (Ghana) guideline

4.1.5 Total Dissolved Solids (TDS)

The TDS of the untreated spent caustic, neutralized caustic and the final effluent were all below 50 mg/l which is the EPA (Ghana) guideline value. The average values of untreated spent caustic, neutralized spent caustic and final effluent were 15.19 mg/l, 0.43 mg/l and 0.04 mg/l. The percentage removal of TDS after neutralization was 76.98% and after wet air oxidation was 92.16%. Figure 4.6 below indicates the plot of sample TDS values and EPA (Ghana) guideline value.

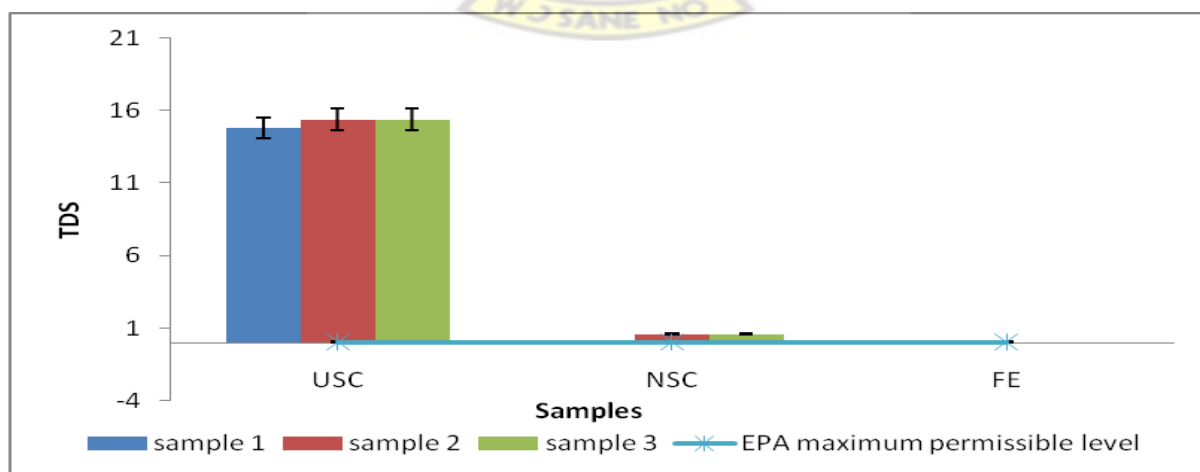


Figure 4.6: plot of TDS values and EPA (Ghana) guideline

4.1.7 Mercaptan (RSH)

The mean mercaptan concentrations in the spent caustic, neutralized spent caustic and final effluent are 368.07 mg/kg, 171.91 mg/kg and 21.13 mg/kg respectively. The mercaptan concentrations reduced by 53.31% after neutralization and 94.26% after wet air oxidation. The Figure 4.7 below is the plot of average RSH values.

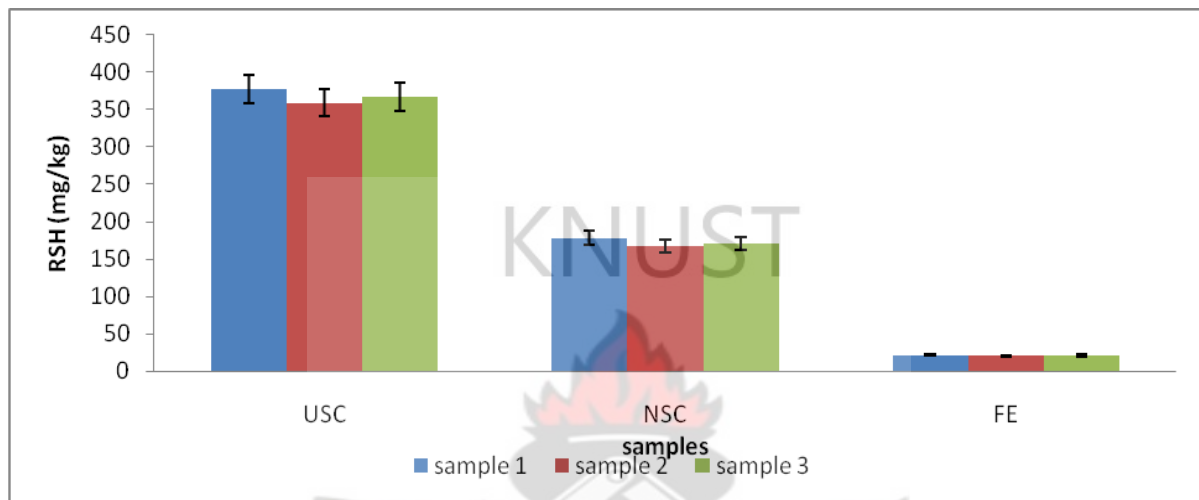


Figure 4.7: Profile RSH values

4.1.6 Hydrogen Sulphide (H₂S)

There was a general reduction in H₂S concentration during treatment. The mean H₂S values of untreated spent caustic, neutralized spent caustic and final effluent are 2157.37 mg/kg, 731.95 mg/kg and 250.47 mg/kg respectively. The removal percentage after neutralization is 66.07% and after wet air oxidation is 88.39%. There is no EPA (Ghana) guideline for H₂S but according to Baker Hughes (2011), death can occur within a few breaths at low concentration of 700 ppm and also deadens the sense of smell at concentration as low as 30 ppm. Figure 4.8 below is the plot of fieldwork H₂S values.

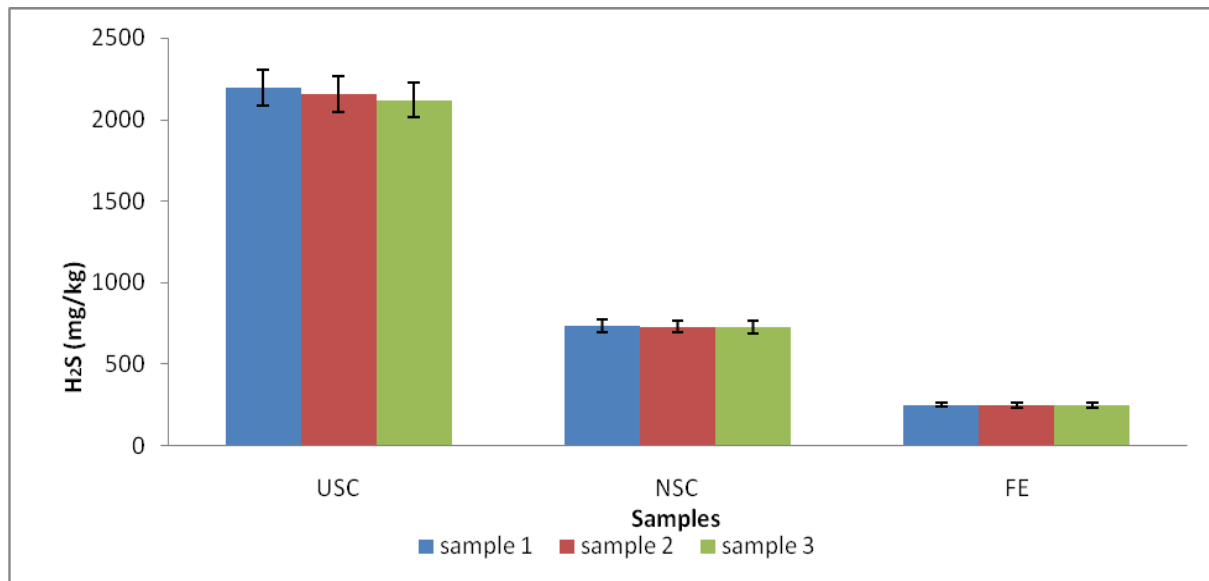


Figure 4.8: Plot of H₂S values

4.2 CORRELATION BETWEEN PARAMETERS

The relationship between two parameters is usually determined using regression analysis and correlation coefficient ' R^2 ' is a critical indicator of such studies. This approach was adopted to assess the correlation among eight variables. Regression analysis for the total data points were carried out using Microsoft Excel and the nature of correlations between parameters were determined based on the correlation coefficients obtained.

4.2.1 Chemical Oxygen Demand (COD) and Biochemical Oxygen of Demand (BOD₅)

From Figure 4.9, COD values increase linearly as BOD₅ also increases. This gave mathematical model of: $COD = 2.147BOD_5 - 141.3$, with an R^2 value of 0.969. The COD and the BOD₅ results obtained showed that the degree of common variation between the variables was highly positively correlated

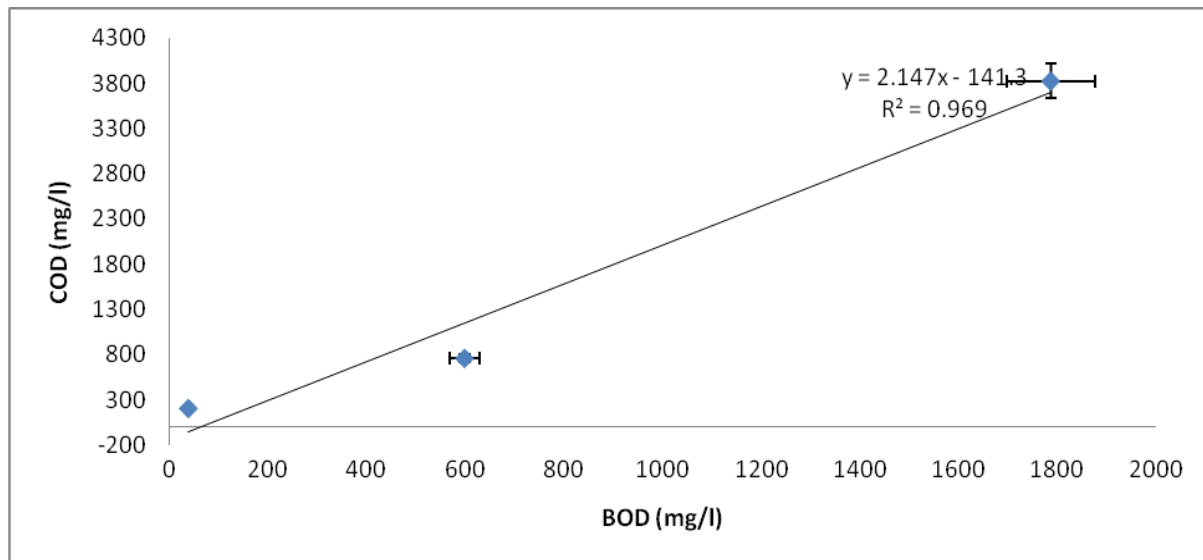


Figure 4.9: Plot of COD versus BOD₅

4.2.2 Chemical Oxygen Demand (COD) and pH

Figure 4.10 below is the plot of COD versus pH. The COD values of the samples increases as pH of the samples also increases. The COD and pH results indicates that the two parameters are highly correlated with R^2 of 0.999 giving a linear equation of $COD = 534.8BOD_5 - 3672$. This high correlation is due to the fact that the factors such as concentrations of carbon dioxide (CO₂), sulphites, sulphates etc that affect COD also affect pH.

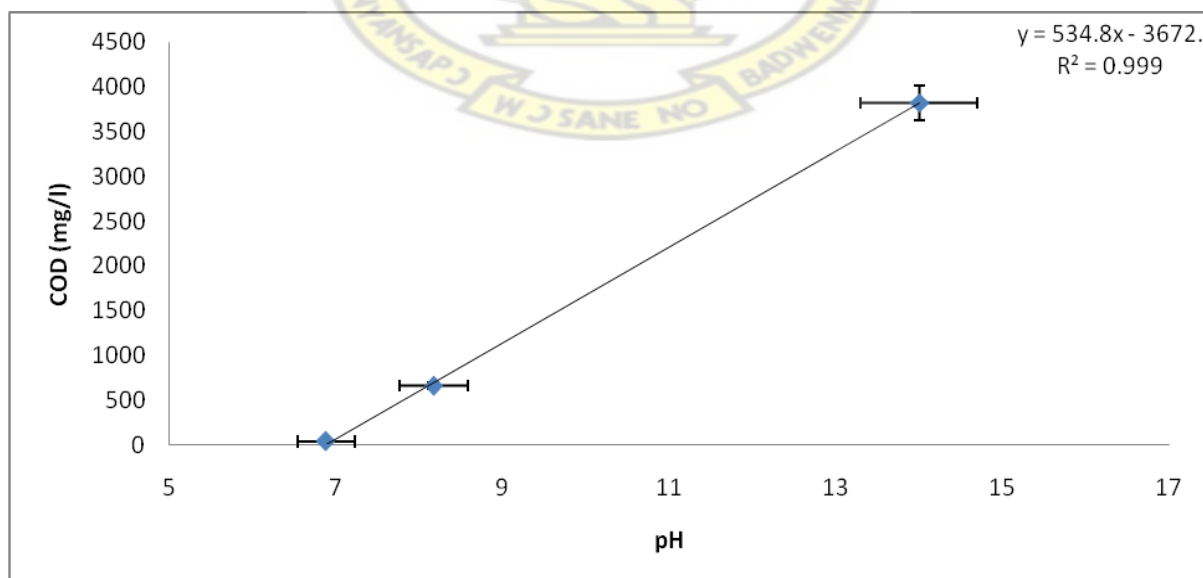


Figure 4.10: Plot of COD versus pH

4.2.3 Phenol and Chemical Oxygen Demand (COD)

The phenol values observed in TOR's spent caustic during analysis have been plotted against the COD as shown in Figure 4.11. This gave mathematical relationship of $\text{Phenol} = 0.468\text{COD} \ln(\text{COD}) - 1.605$ with R^2 of 0.963. The phenol and the COD results obtained showed that the degree of common variation between the variables was highly positive though the deviation of the points are large. This means that the phenol and the COD may be correlated and this may indicate that certain substances such as conjugate ring compounds are common to both species.

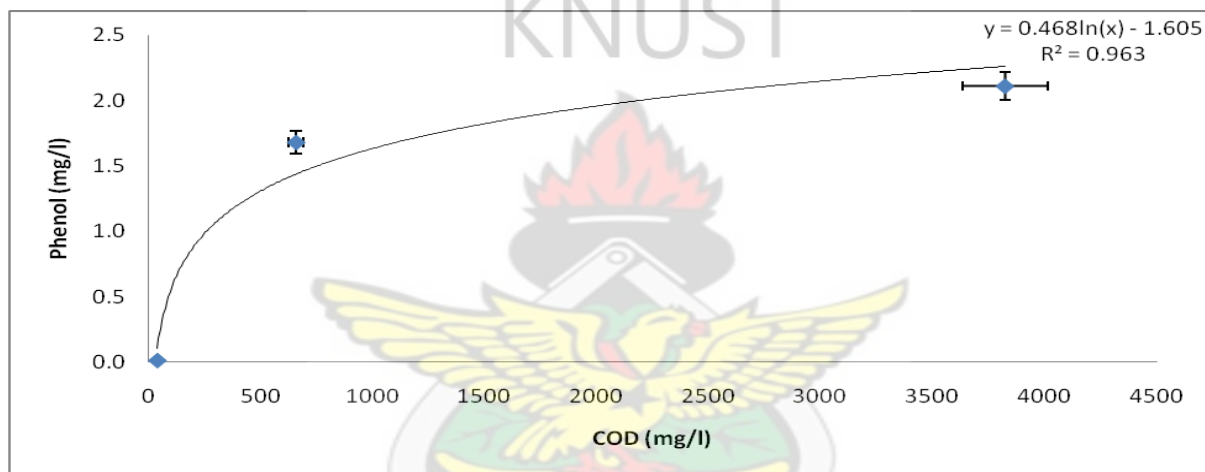


Figure 4.11: Profile of phenol versus COD

4.2.4 Total Dissolved Solids (TDS) and Chemical Oxygen Demand (COD)

A plot of TDS versus COD gives a very good correlation showing that as TDS increases COD also increase. As in Akan *et al* (2009) investigation, such correlation shows that levels of TDS and COD are affected by same activities such as heavy metals pollution within the study area. From Figure 4.12, $R^2 = 1$ with polynomial equation of $\text{TDS} = 10^{-06}\text{COD}^2 + 0.042$.

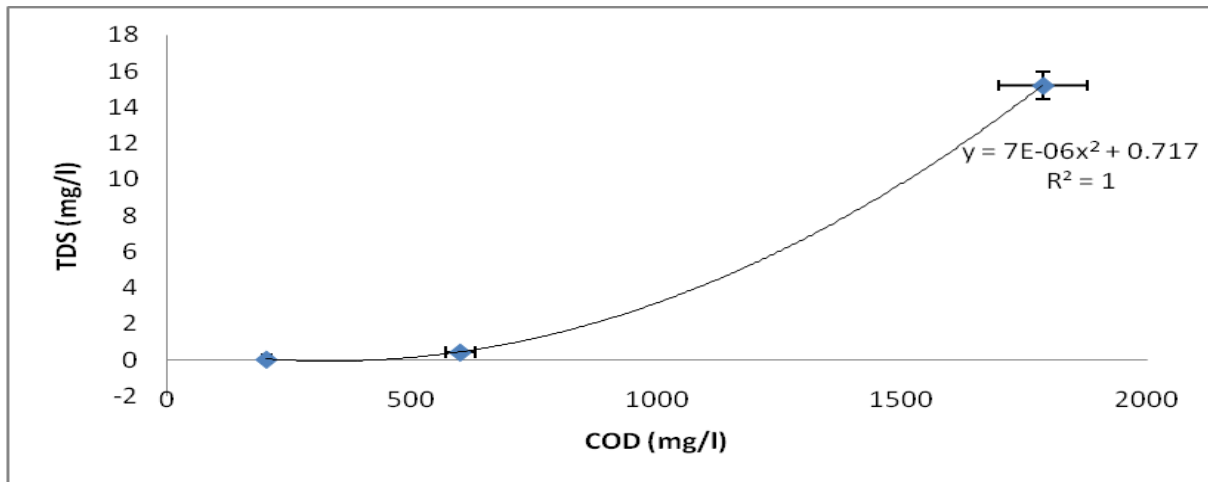


Figure 4.12: Plot of TDS versus COD

4.2.5 Total Suspended Solids (TSS) and Chemical Oxygen Demand (COD)

Figure 4.13 shows the plot of TSS against COD. This plot gives a very good linear correlation with $R^2 = 0.999$ and model equation of $TSS = 0.008COD + 6.515$.

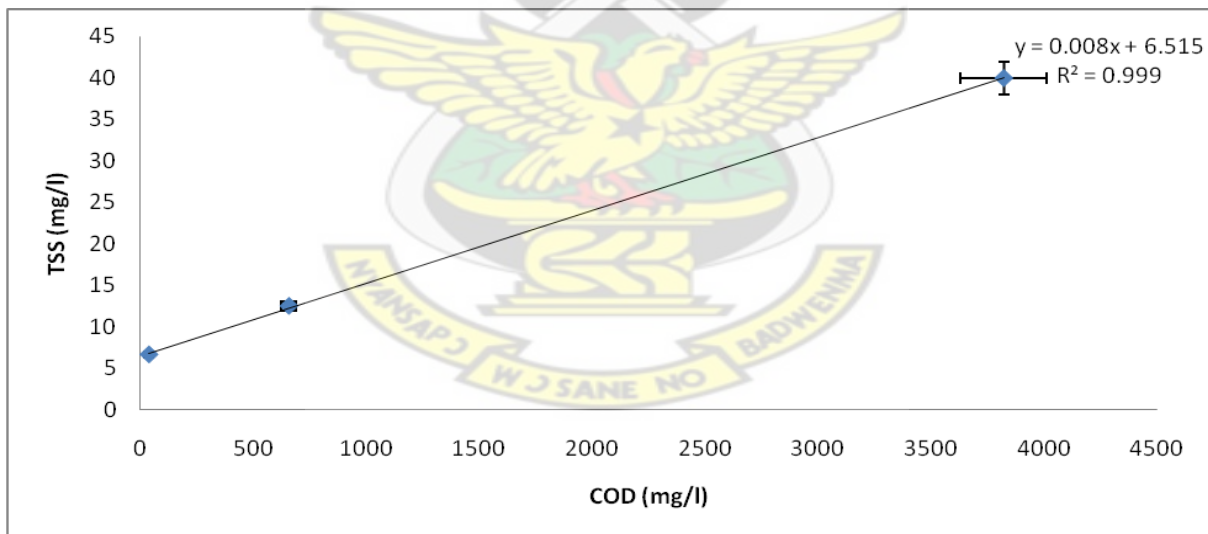


Figure 4.13: Plot of TSS versus COD

4.2.6 Mercaptans (RSH) and Chemical Oxygen Demand (COD)

Figure 4.14 below is the plot of RSH versus COD. The TSS and COD results indicates that the two parameters are highly correlated with R^2 of 0.994 and an equation of $RSH =$

159.7lnCOD-835.4. This high correlation may be due to the fact that the factors like sulphides affect both parameters.

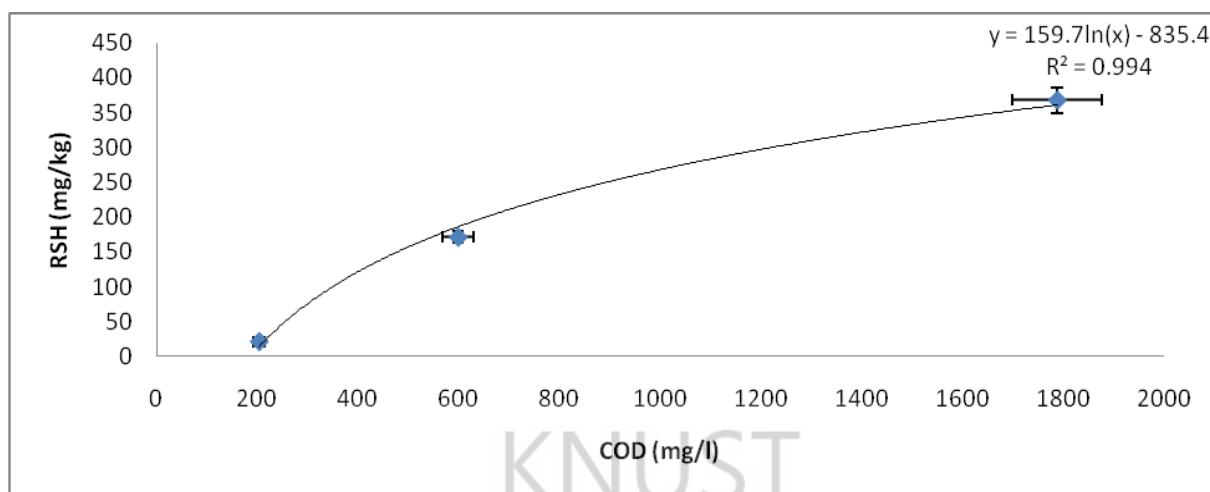


Figure 4.14: Plot of RSH versus COD

4.2.7 Hydrogen Sulphide (H₂S) and Chemical Oxygen Demand (COD)

A profile of H₂S versus COD gives a very good correlation showing that as H₂S increases COD also increase. As in Akan *et al* (2009) investigation, such correlation shows that levels of H₂S and COD are affected by same activities like heavy metal and salt pollution within the study area. From Figure 4.15, $R^2 = 0.991$ with linear equation of $H_2S = 0.486COD + 313.8$.

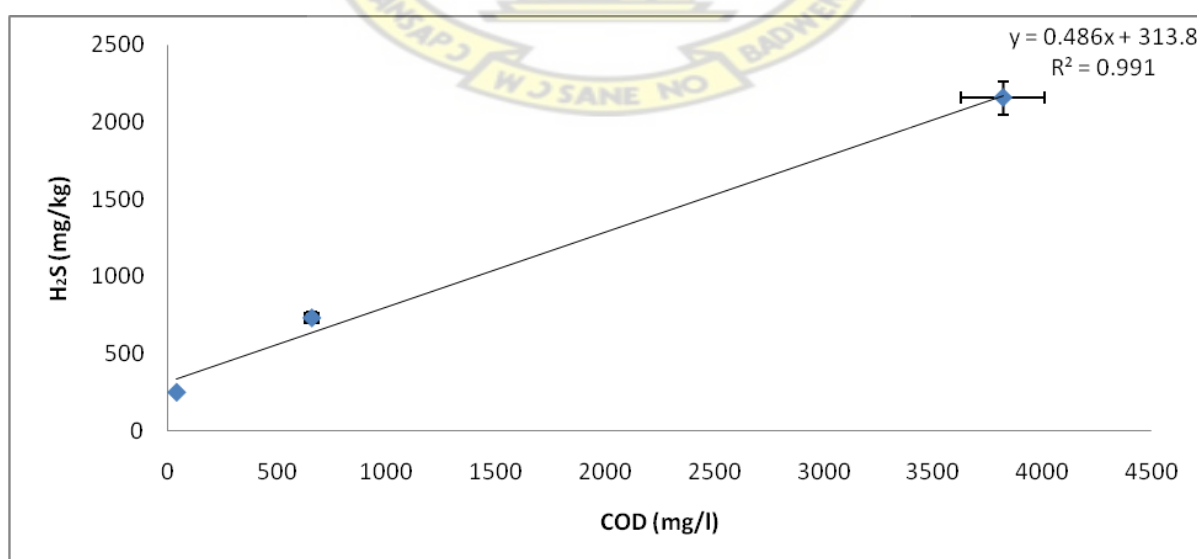


Figure 4.15: Plot of H₂S versus COD

4.2.8 Biochemical Oxygen Demand (BOD₅) and pH

Figure 4.16 below is the plot of BOD₅ against pH which shows a very good correlation which is highly positive. This gave an equation of $BOD_5 = 216.9pH - 1236$ with a corresponding R^2 value of 0.995.

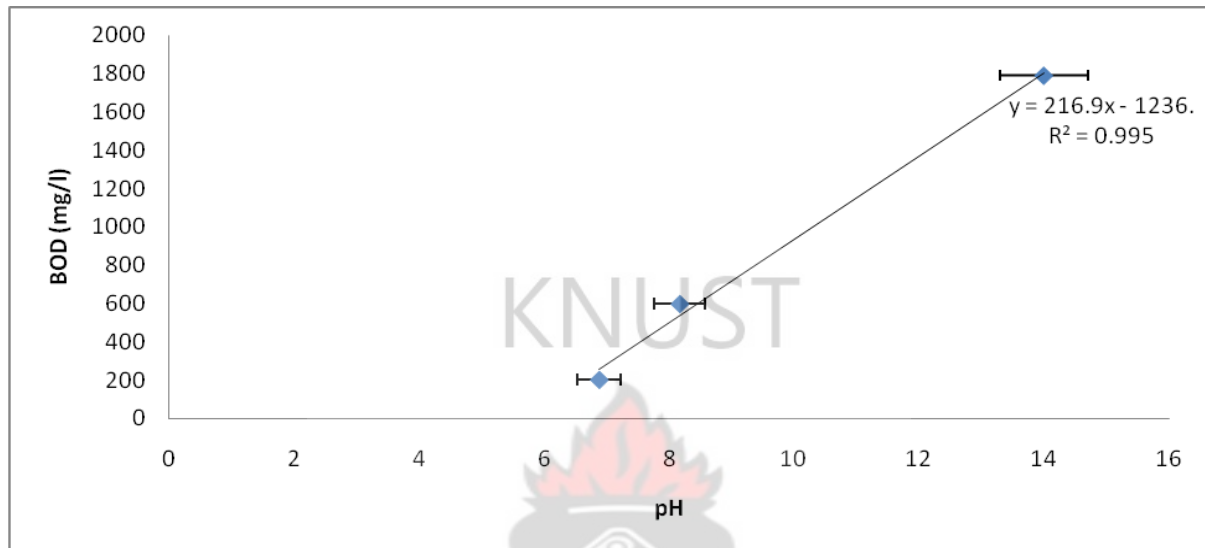


Figure 4.16: Profile of BOD₅ versus pH

4.2.9 Total Dissolved Solids (TDS) and Biochemical Oxygen Demand (BOD₅)

In Figure 4.17, the plot indicates that as TDS decreases BOD₅ also decrease. This could be that there is/are constituents in the spent caustic solution which affect both TDS and BOD₅. The R^2 is 1 which is highly positive with the equation of $TDS = 7 \times 10^{-6} BOD_5^2 - 0.004 BOD_5 + 0.717$.

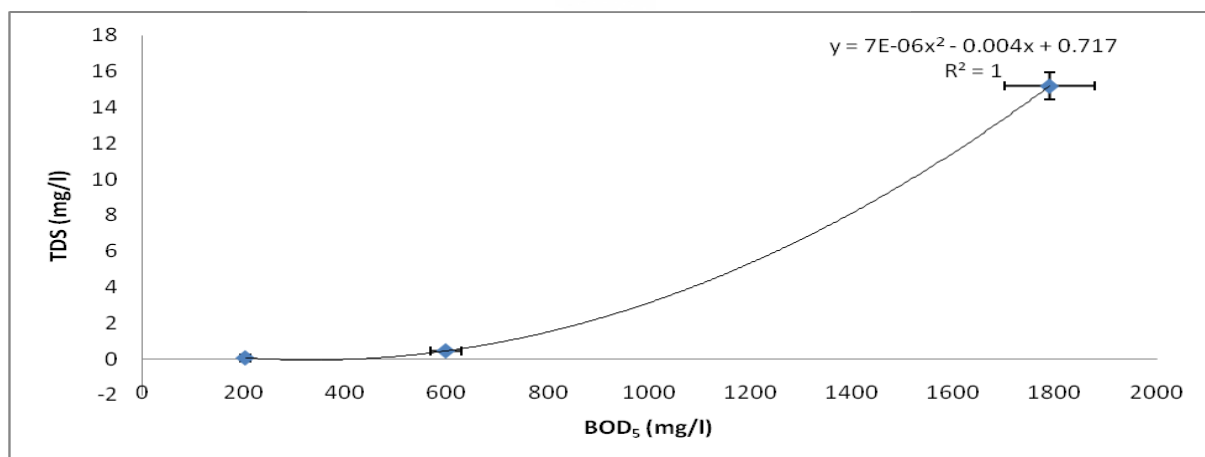


Figure 4.17: Plot of TDS versus BOD₅

4.2.10 Total Suspended Solids (TSS) and Biochemical Oxygen Demand (BOD₅)

The plot of TSS and BOD₅ gave a linear equation of $TSS = 0.021BOD_5 + 1.156$ with R^2 of 0.994 which is highly positive. Figure 4.18 can be explained by the fact that TSS and BOD₅ have certain things organic compounds like benzene and toluene in common which are responsible for this linear correlation. This is because TSS can lead to the development of sludge deposits and anaerobic conditions in an untreated wastewater.

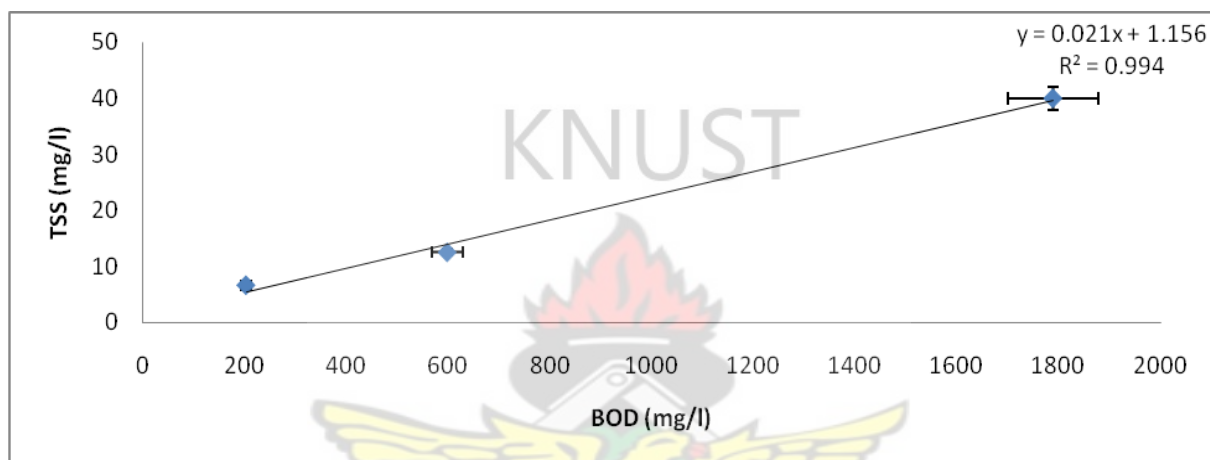


Figure 4.18: Plot of TSS versus BOD₅

4.2.11 Hydrogen Sulphide (H₂S) and Biochemical Oxygen Demand (BOD₅)

The correlation between H₂S and BOD₅ is highly positive with R^2 of 1 which is a perfect value with the equation of $H_2S = -10^{-05}BOD^2 + 1.227BOD_5 + 1.116$. According to Al-Ali (2011), sulphate/sulphide compounds usually have poor correlation with BOD₅ but this is at variance with the finding here in that while aerobic bacteria in the wastewater use the available oxygen to increase BOD₅ sulphur reducing bacteria convert sulphate into hydrogen sulphide without using oxygen.

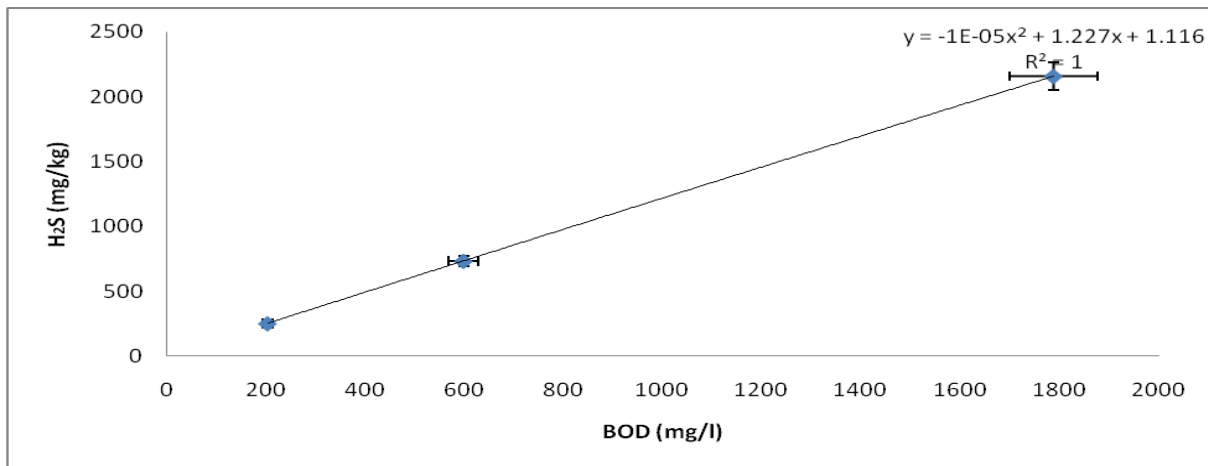


Figure 4.19: Plot of H₂S versus BOD₅

4.2.12 Phenol and Biochemical Oxygen Demand (BOD₅)

Figure 4.20 shows the correlation between phenol and BOD₅ with R^2 of 0.893 and an equation of Phenol = $0.964\ln\text{BOD}_5 - 4.908$. This high correlation may be due the presence of conjugate ring compounds like benzene and toluene in the solution. The accumulation of organic constituents increases BOD₅ well as phenol concentration.

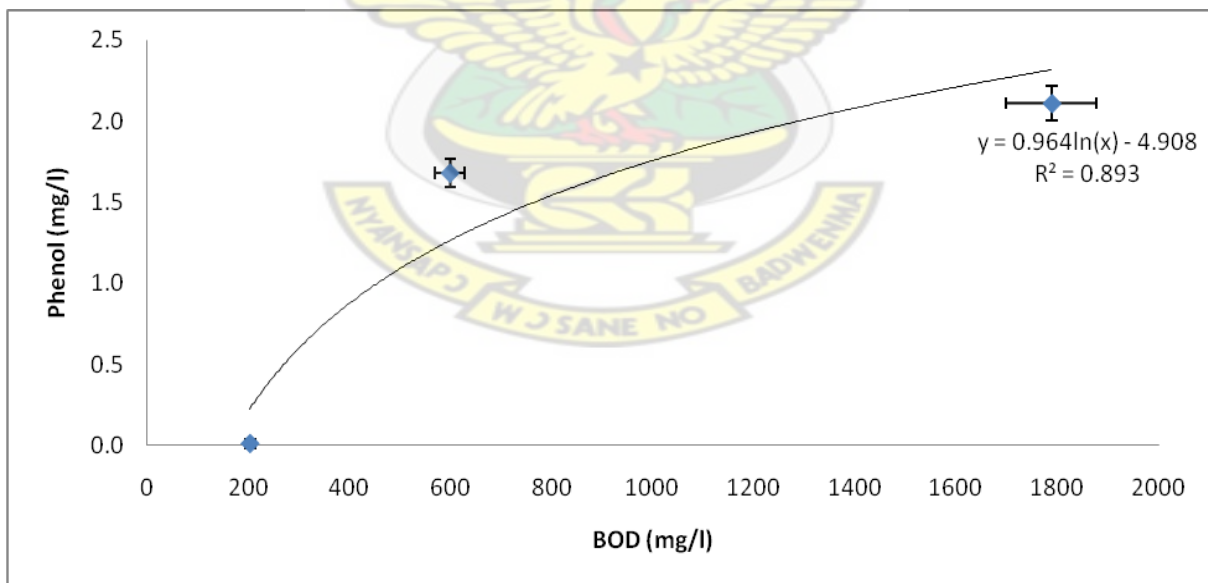


Figure 4.20: Plot of Phenol versus BOD₅

4.2.13 Mercaptan (RSH) and Biochemical Oxygen Demand (BOD₅)

From Figure 4.21, BOD₅ increases as RSH increases and the correlation between them is positive with R^2 value 1 and an exponential equation of $BOD_5 = -5 \times 10^{-5}(RSH)^2 + 0.275RSH + 10.65$. The results show a reverse finding to that of Al-Ali (2011) finding. This may be due to the fact that while sulphur reducing bacteria (SRB) converts sulphates and sulphites into hydrogen sulphide (H₂S) and mercaptans (RSH) without using oxygen, aerobic bacteria that may be present were being poisoned by the SRB products after the attainment of the threshold value of 410 mg/l RSH.

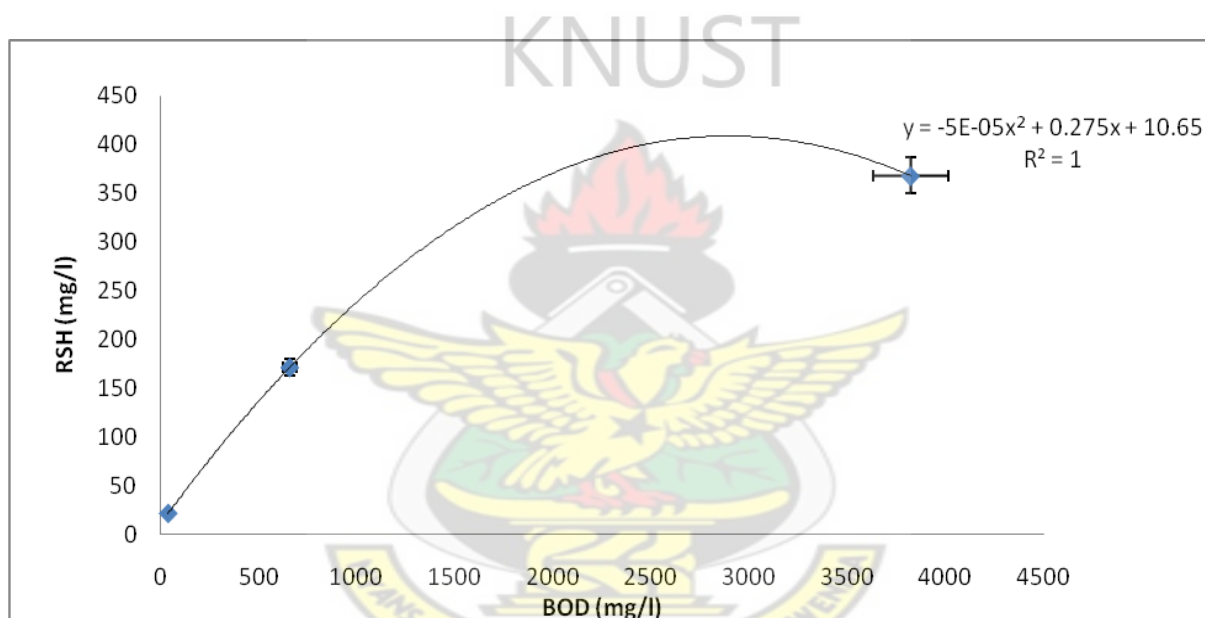


Figure 4.21: Plot of RSH versus BOD₅

4.2.14 Total Dissolved Solids (TDS) and pH

The plot of TDS against pH yields a linear correlation with an equation of $TDS = 2.251pH - 16.58$ giving R^2 of 0.978. This correlation is highly positive which is suggesting that compounds like chlorides, sulphates, nitrates, iron etc responsible for TDS increment are also accountable for pH increment in similar situation.

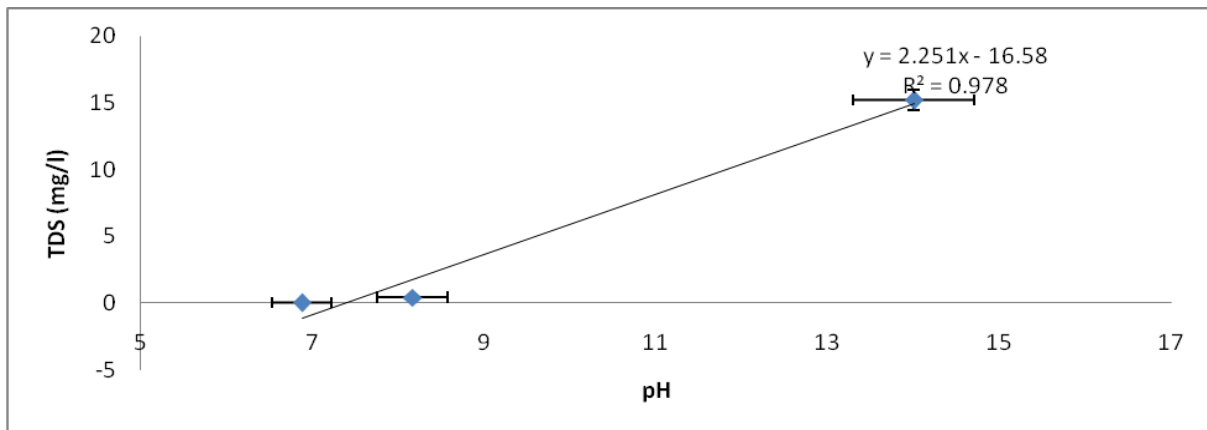


Figure 4.22: Plot of TDS versus pH

4.2.15 Total Suspended Solids (TSS) and pH

Logarithmically, TSS increases as pH increases. Figure 4.23 shows the plot of TSS against pH with an equation of $TSS = 47.80 \ln(\text{pH}) - 86.55$ giving R^2 of 0.995.

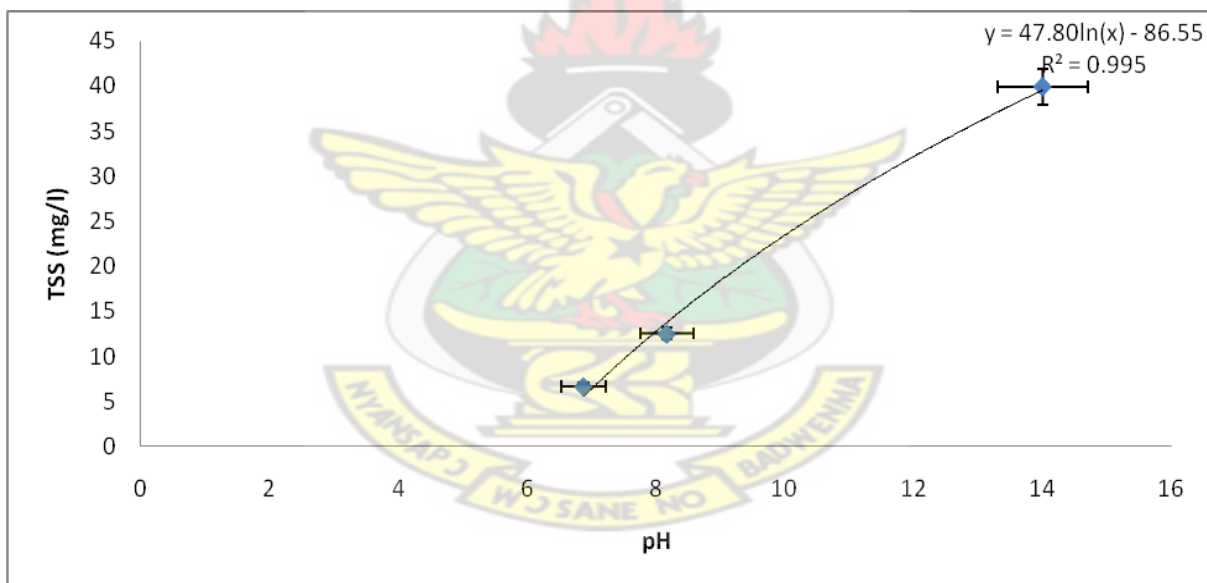


Figure 4.23: Plot of TSS versus pH

4.2.16 Phenol and pH

Figure 4.24 shows the correlation between phenol and pH. Initial increment of 1.66 mg/l gives a relatively insignificant change in pH value of 1.29 where as a further increase of 0.44 mg/l of phenol causes the pH change to a maximum of 14. Therefore suggesting two stage transformational relationship

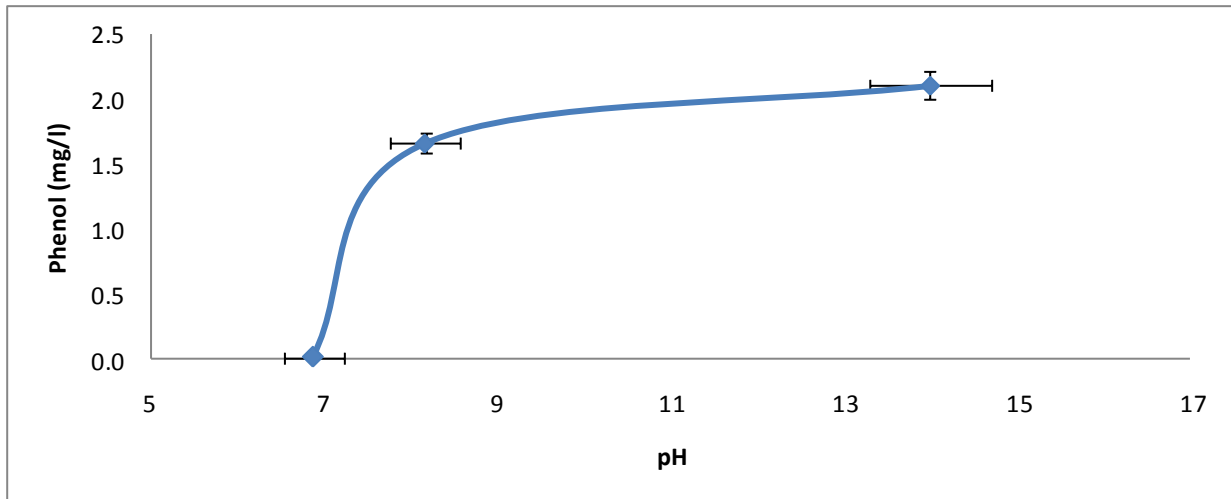


Figure 4.24: Plot of Phenol versus pH

4.2.17 Hydrogen Sulphide (H₂S) and pH

The plot of TDS against pH is linear in nature giving an equation of $H_2S = 260.6pH - 1477$ with R^2 of 0.994 shown in Figure 4.25. This highly positive correlation suggests that the factors (sulphides and sulphates) responsible for H₂S increment are also responsible for pH increment.

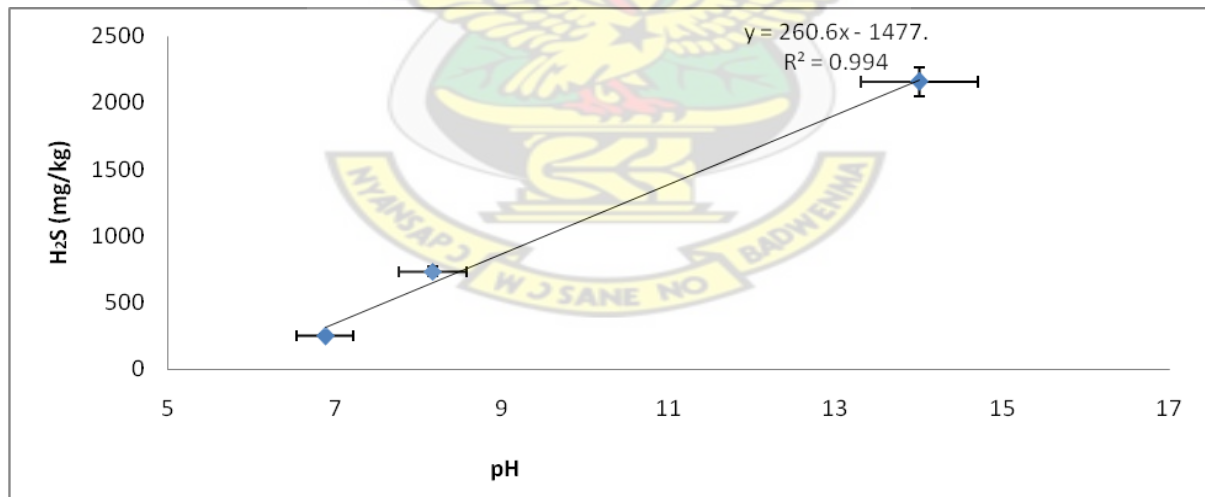


Figure 4.25: Plot of H₂S versus pH

4.2.18 Mercaptan (RSH) and pH

The plot of mercaptan (RSH) against pH linearly gave an equation of $RSH = 44.12pH - 240.1$ with R^2 of 0.925. This correlation is highly positive which suggests that the factors (sulphates

Treatment and Disposal of Spent Caustic at TOR

sulphides, benzene and toluene) responsible for RSH increment are also responsible for pH increment.

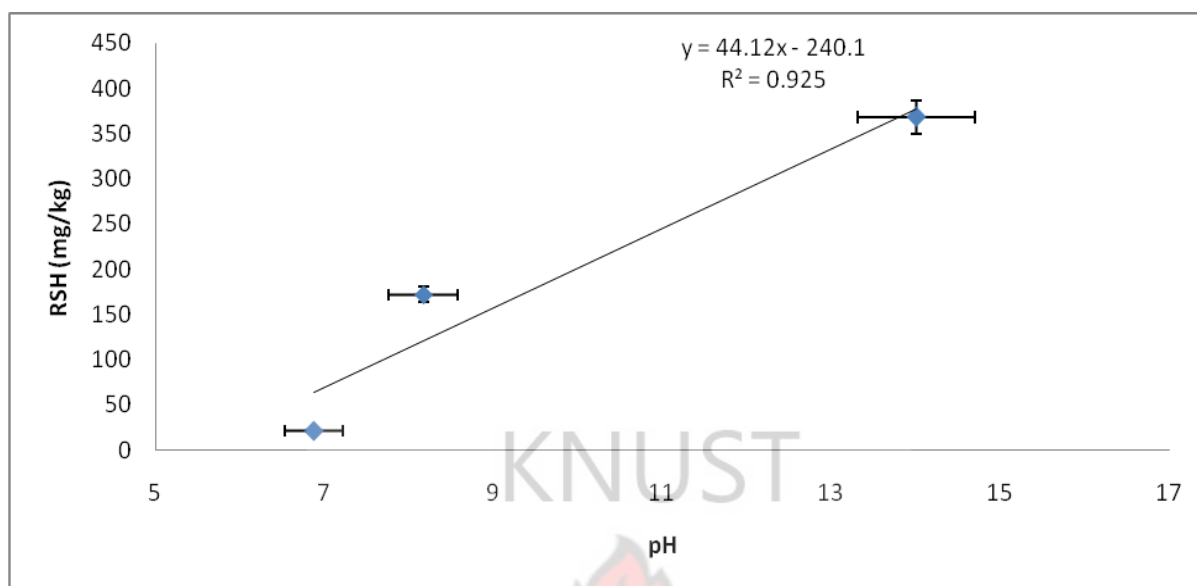
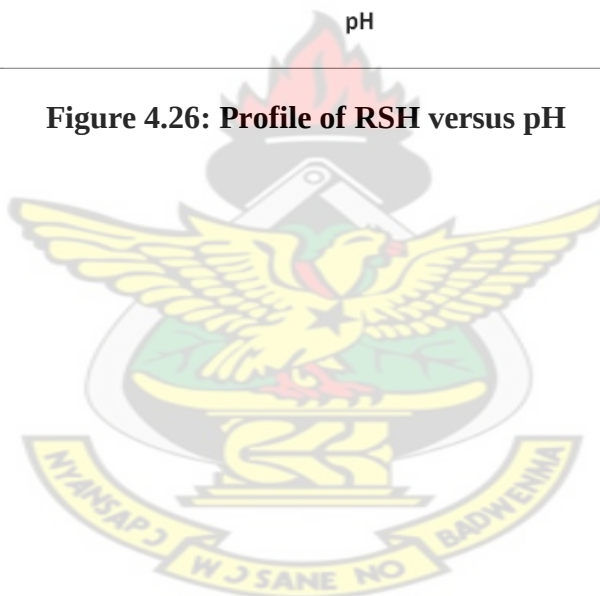


Figure 4.26: Profile of RSH versus pH



CHAPTER FIVE

5.0 CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

This study has established that the treatment of TOR's spent caustic solution using a two stage process of acid neutralization followed by wet air oxidation (WAO) is the most effective treatment prescription. This sequence of operation allows onsite treatment without producing odourous off-gas and is able to effectively treat the effluent to a level lower than the EPA guidelines specification for that sector.

Over the two stage process, 88.46% of hydrogen sulphide (H_2S) was removed while 99.57% of phenol and 94.33% of mercaptans were also removed. Also pH, COD, BOD_5 , TDS and TSS values were reduced by 50.93%, 88.97%, 99.03%, 99.73% and 84.37% respectively. The resulting effluent, thus are within the EPA (Ghana) permissible levels.

This study is suggesting the existence of interrelationships among some physico-chemical wastewater indicators whereby reliable correlations have been deduced using statistical analysis. This suggests that it may be possible to predict the levels of contamination by measuring a few critical parameters.

5.2 RECOMMENDATIONS

The spent caustic tank at TOR should be cleaned with time to reduce the COD load on the waste water treatment plant.

It is also recommended that separate plants (neutralization and wet air oxidation plant) should be set up to effectively treat spent caustic at TOR to an acceptable standard.

The suggested correlations and their equations will have to be consolidated with further research in this area.



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APPENDICES

Treatment and Disposal of Spent Caustic at TOR

APPENDIX A – DETAILED LABORATORY RESULTS

A.1 SAMPLE1 ANALYSIS

Parameter	unit	Untreated spent caustic	Average	After neutralization of spent caustic	Average	After WAO	Average	Error analysis		
pH		14	14.00	8	8.67	7	6.87	USC	NSC	FE
		14		9	-3.85	6.8	0.13			
		14		9	0.67	6.8				
BOD ₅	ppm	1752.02	1,753.34	580.45	603.64	40.44	38.52	0.075285	3.842225	3.539084
		1820.22		640.24		38.28		-3.81443	-6.06	-1.37453
		1687.78		590.24		36.86		3.739149	2.220406	-2.16456
COD	ppm	3870.5	3,838.95	680.24	653.37	200.24	207.59	-0.82184	-4.11199	-4.99351
		4020.55		645.23		210.44		-4.73046	1.246352	0.614453
		3625.8		634.65		212.08		5.552299	2.865641	4.379057
PHENOL	ppm	3	2.33	2	1.83	0.01	0.01	-28.5714		
		2		1.5		0.01		14.28571		
		2		2		0.01		14.28571		
H ₂ S	mg/kg	2282.4026	2,197.19	735.2784	735.55	252.3842	254.50			
		2280.5024		750.4884		260.8824				
		2028.6542		720.8842		250.2422				
RSH	mg/kg	350.2242	378.04	162.6428	178.39	22.5426	21.43			
		382.6486		182.5427		20.8274				
		401.2348		189.9842		20.9287				
TDS	m/s	14.5	14.80	0.1	0.11	0.04	0.04			
		15.1		0.12		0.045				
		14.8		0.11		0.038				
TSS	ppm	42	40.33	13	12.50	8	7.33			
		40		13		7				
		39		12		7				

Treatment and Disposal of Spent Caustic at TOR

A.2 SAMPLE 2 ANALYSIS

Parameter	Unit	Untreated Spent Caustic	Average	After Neutralization process	Average	After WAO	Average
pH		14	14.00	8	8.00	7	6.87
		14		8		6.8	
		14		8		6.8	
BOD ₅	ppm	1864.42	1,824.99	581.56	601.30	40.1	37.39
		1823.34		640.66		36.38	
		1787.22		581.69		35.78	
COD	ppm	3882.5	3,844.00	680.86	651.85	208.64	205.75
		3924.24		650.24		198.34	
		3725.25		624.44		210.28	
PHENOL	ppm	2	2.00	2	1.67	0.01	0.01
		2		1.5		0.01	
		2		1.5		0.01	
H ₂ S	mg/kg	2244.342	2,155.76	734.3748	731.96	242.4852	248.87
		2108.253		740.8424		252.6842	
		2114.682		720.6642		251.4264	
RSH	mg/kg	364.2446	359.23	163.4828	166.97	21.2648	20.61
		354.8921		172.4275		20.4484	
		358.5645		164.9852		20.1248	
TDS	m/s	14.8	15.37	0.11	0.60	0.038	0.04
		15.7		0.9		0.041	
		15.6		0.8		0.036	
TSS	ppm	40	39.33	12	12.33	6	6.33
		37		13		6	
		41		12		7	

Treatment and Disposal of Spent Caustic at TOR

A.3 SAMPLE 3 ANALYSIS

Parameter	Unit	Untreated spent caustic	Average	After neutralization	Average	After WAO	AVERAGE	pH	USC	NSC	FE
pH		14	14.00	8	7.83	6.8	6.90		14	8.67	6.87
		14		7.6		6.9			14	8.00	6.87
		14		7.9		7			14	7.80	6.90
BOD ₅	ppm	1765.64	1,786.77	590.64	591.32	39.21	38.96		9	9	9
		1802.42		620.89		37.82			6	6	6
		1792.24		562.42		39.86			14	8.16	6.88
COD	ppm	3682.6	3,783.09	642.42	668.10	188.34	197.15				
		3822.42		689.34		200.64					
		3844.25		672.54		202.48					
PHENOL	ppm	2	2.00	1.8	1.50	0.01	0.01				
		2		1.4		0.01					
		2		1.3		0.01					
H ₂ S	mg/kg	2132.4223	2,119.12	722.3834	728.05	239.8452	248.03				
		2200.2565		750.82451		261.3822					
		2024.6842		710.9282		242.8673					
RSH	mg/kg	374.4264	367.26	174.7482	170.37	22.2243	21.34				
		367.8874		168.7482		21.5484					
		359.4784		167.6245		20.2482					
TDS	ppm	15.2	15.40	0.12	0.59	0.029	0.03				
		15.2		0.8		0.032					

Treatment and Disposal of Spent Caustic at TOR

		15.4		0.85		0.034					
TSS	ppm	41.12	41.33	13	12.67	7	6.33				
		41.23		12		6					
		41.64		13		6					

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Treatment and Disposal of Spent Caustic at TOR

A.4 AVERAGES OF VARIOUS TESTS

BOD ₅	3838.95	3844.00	3783.09
	653.37	651.85	668.10
	205.59	205.70	195.15
pH	14.00	14.00	14.00
	8.67	8.00	7.83
	6.87	6.87	6.90
Phenol	2.33	2.00	2.00
	1.83	1.67	1.50
	0.01	0.01	0.01
H ₂ S	2197.19	2155.76	2119.12
	735.55	731.95	728.05
	254.50	248.87	248.03
RSH	378.04	359.23	367.26
	178.39	166.97	170.37
	21.43	20.61	21.34
TDS	14.80	15.37	15.40
	0.11	0.60	0.59
	0.04	0.04	0.03
TSS	40.33	39.33	40.12
	12.50	12.33	12.67
	7.33	6.33	6.33

Treatment and Disposal of Spent Caustic at TOR

A.5 PERCENTAGE REDUCTION AFTER NEUTRALIZATION AND WAO

		After WAO	After WAO				
Phenol	Sample 1	21.46	99.57	H ₂ S	Sample1	66.51	88.42
	Sample 2	16.50	99.50		Sample 2	66.05	88.46
	Sample 3	25.00	99.50		Sample 3	65.64	88.30
RSH	Sample 1	52.81	94.33	BOD ₅	Sample 1	82.98	99.00
	Sample 2	53.52	94.26		Sample 2	83.04	99.03
	Sample 3	53.61	94.19		Sample 3	84.37	94.79
TDS	Sample 1	99.26	99.73	COD	Sample 1	65.57	88.16
	Sample 2	66.05	88.46		Sample 2	67.05	88.73
	Sample 3	65.64	88.30		Sample 3	66.91	88.97
TSS	Sample 1	69.01	81.82				
	Sample 2	68.65	83.91				
	Sample 3	69.37	84.37				
pH	Sample 1	38.07	50.93				
	Sample 2	42.86	50.93				
	Sample 3	44.29	50.71				

Treatment and Disposal of Spent Caustic at TOR

APPENDIX B - ENVIRONMENTAL GUIDELINES FOR INDUSTRY IN GHANA GHANA EPA SECTOR SPECIFIC EFFLUENT QUALITY GUIDELINES FOR DISCHARGES INTO NATURAL WATER BODIES (MAXIMUM PERMISSIBLE VALUES)

PARAMETER	Oil and Gas Exploration, Production and Refining
pH	6-9
BOD ₅ (mg/l)	50
Oil & Grease	10
Total Dissolved Solids (mg/l)	50
Total Suspended Solids (mg/l)	50
Cadmium (mg/l)	0.1
Total Phosphorus (mg/l)	2.0
Temperature increase	<3°C above ambient
Colour (TUC)	200
COD (mg/l)	250
Chromium (+6) (mg/l)	0.1
Sulphide (mg/l)	1.0
Phenol (mg/l)	0.5
Total Coliforms (MPN/100ml)	400
E. Coli (MPN/100ml)	0
Turbidity (N. T. U)	75
Lead (µg/l)	0.1
Nitrate (mg/l)	2
Total Phosphorus (mg/l)	75
Conductivity (µS/cm)	750
Mercury (µg/l)	10
Zinc (mg/l)	2.0
Tin (mg/l)	-
Total Chromium (mg/l)	0.5
Total Iron (mg/l)	2
Free Cyanide (mg/l)	-
Cyanide as Weak Acid Dissociable (mg/l)	-

APPENDIX C - PUBLICATION

BENCH-SCALE TREATMENT OF SPENT CAUSTIC SOLUTION FROM OIL REFINERY – A Case Study at Tema Oil Refinery in Ghana

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ABSTRACT

Handling of spent caustic solution at the refinery sites mostly creates problems during the treatment in biological treatment plants due high chemical oxygen demand (COD) and pH. The research focused on the treatment of spent caustic from Tema Oil Refinery (TOR) before disposal. The methods of treatment used are acid neutralization and Wet Air Oxidation (WAO). Treatment of high concentration chemical wastewater obtained from petrochemical company by acid neutralization and Wet Air Oxidation (WAO) was studied. The chemical of concern in the spent caustic wastewater included reduced sulphur compounds such as sulphides and mercaptans as well as organic species such as sodium salts of phenols, nepththenic and cresylic acid. Due to the types of chemicals contained in spent caustic, the spent caustic wastewater can be environmentally hazardous and difficult to treat. Acid neutralization reduced majority of COD and foaming tendency by removing sulphides and nepththenic acid but not phenols or produce biodegradable effluent. High temperature wet air oxidation oxidized all reduced sulphur compounds and phenols, eliminated the foaming tendency of the spent caustic and reduced a majority of the COD to produce biodegradable effluent. Laboratory and field data have been presented to show the effectiveness of wet air oxidation for treating the spent caustic wastewater.

INTRODUCTION

Sodium hydroxide (caustic) scrubbing solutions are commonly used in petrochemical and petroleum refineries for the removal of acid components such as hydrogen sulphide (H_2S), cresylic acids, mercaptans and naphthenic acids from the refined product streams. When the sodium hydroxide is used in the plant to remove hydrogen sulphide (H_2S), mercaptans, cresylic etc, the resulting waste is called spent caustic soda. Once spent, the caustic solutions can be a challenge to handle and dispose of (Kumfer, Chad and Clay, 2010). Spent caustic typically have a pH greater than 12, sulphide concentrations exceeding 2 – 3 wt%, and about 80% of residual alkalinity. Depending on the source, spent caustics might contain, for example, mercaptans, H_2S , thiols, phenols, and amines (Kolhatkar and Sublette, 1996).

Treatment Methods

The three main available treatment methods for spent caustic treatment are; Wet Air Oxidation, acid neutralization and the use of Fenton's reagent

According to Teletzke, 1996, the wet oxidation reactions take place between 100 and 372 °C at elevated pressures to maintain water in the liquid phase. This temperature range can be further subdivided into low (100 - 200 °C), medium (200 - 260 °C), and high temperature (260 - 320 °C) operation. Higher temperature (320 - 372 °C) systems can be designed as well but are rarely used.

In the acid neutralization treatment process, the spent caustic wastewater is acidified to release acidic components that were captured in the alkaline caustic solution. This results in sulphides and mercaptans being released as acid gases and naphthenic acids to be sprung as an oil layer. One large differentiation between acid neutralization and WAO is that the acid components in the spent caustic are removed but not destroyed. In some cases this results in additional treatment to be required. In others it allows for the capture and re-use of some of the components in the spent caustic.

Fenton's reagent ($\text{Fe}^{2+} / \text{H}_2\text{O}_2$) can oxidize refractory pollutants at a low temperature and pressure (Lin *et al.*, 1999). But due to a high COD value of spent caustic, it consumes a large amount of H_2O_2 . Also, because of a high concentration of H_2S (up to 20 g/l), its reaction with ferric ion causes a loss of iron catalyst activity. The spent caustic is first neutralized with sulphuric acid to pH=5.0. Fenton's reagent is then added to oxidize the solution. As a result, the spent caustic treatment becomes economical and effective. (Shih-Hsung S. and Hung-Shan W, 2000).

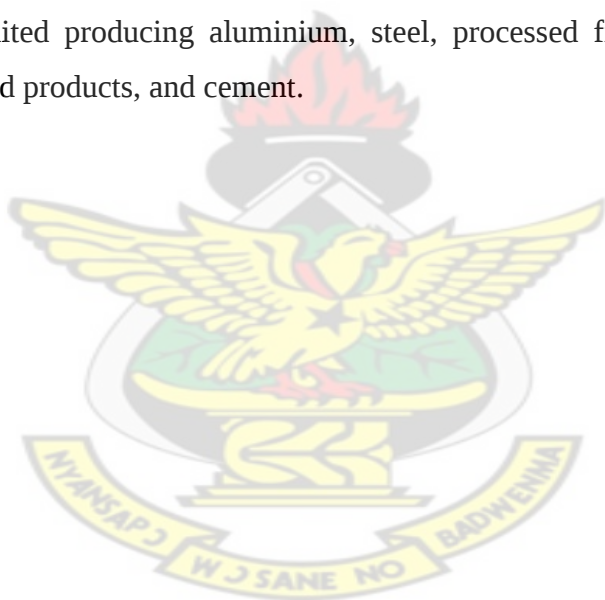
Treatment and Disposal of Spent Caustic at TOR

In this study, acid neutralization and wet air oxidation were used to treat refinery spent caustic to an acceptable levels with the research objectives being the studying the usage of caustic soda in the plant, analyzing the nature and form of the residues and designing a treatment method for treating the spent caustic soda.

MATERIALS AND METHODOLOGY

Description of the Study Site

Tema is a town on the Atlantic Coast of Ghana. It is located 25 km east of the national capital, Accra, in greater Accra region. The Greenwich meridian passes directly through the town. Major companies operating in Tema include Volta Aluminium Company Ltd. (VALCO), Tema Oil Refinery (TOR), Nestlé Ghana Ltd, Ghana Cement Works (GHACEM) and Sentuo Steel Limited producing aluminium, steel, processed fish, refined petroleum, textiles, chemicals, food products, and cement.



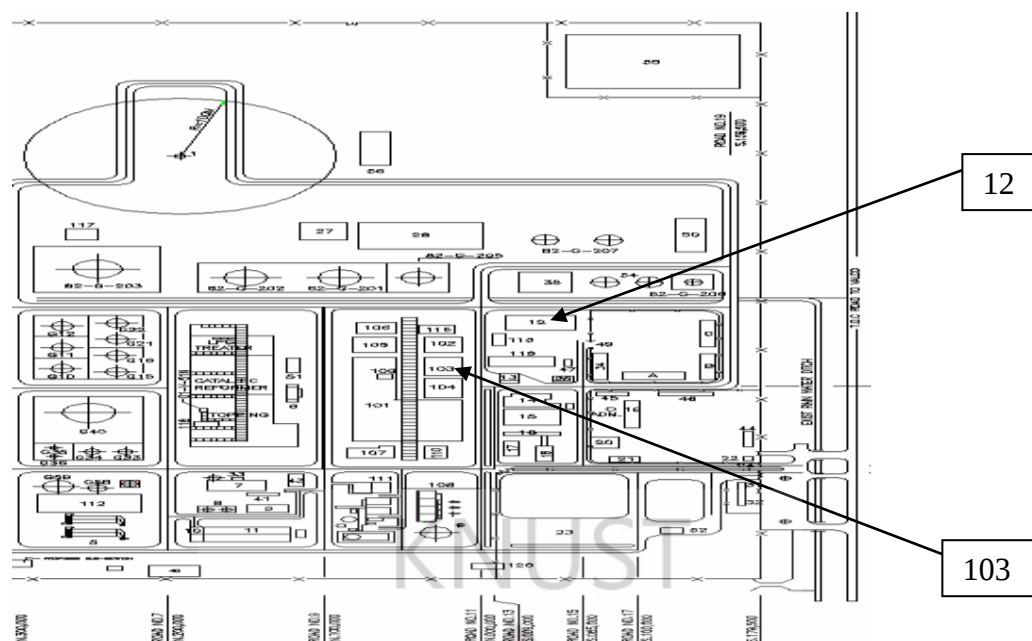


Figure 1 Site Plan of Tema Oil Refinery (TOR) (Code 103 is Sampling point and Code 12 is Quality Control laboratory)

EXPERIMENTAL PROCEDURE

Acid neutralization

Acid neutralization testing was performed using concentrated hydrochloric acid to adjust the pH to <9 by the process of titration.

Wet Air Oxidation

Laboratory autoclave was used to perform WAO testing. Spent caustic was placed into an autoclave and charged with compressed air. The volume of air was controlled by pressure valves. The autoclave was held at a temperature of 250°C for a reaction time of 40 minutes.

Analysis of Samples

Determination of sampling methodology was tested using both grab sampling method and composite sampling method in order to test the suitability of each sampling method or otherwise. Composite sampling was preferred over grab sampling in order to ensure homogeneity of samples.

Treatment and Disposal of Spent Caustic at TOR

Parameters that were analysed for are pH, phenol, RSH/H₂S, BOD₅ COD, TDS and TSS for each sample taken.

The pH of the solutions was determined using OAKTON pH meter with the sensitivity level of ± 0.01 .

Phenol concentrations were determined using direct photometric method according to American Society for Testing and Materials (ASTM) D1783 -01.

Sulphur and mercaptan concentrations were determined using the Universal Oil Products (UOP) 163-10 test method.

The Biochemical Oxygen Demand (BOD₅) was determined using the respirometric method according to International Standard Organization (ISO) 5815. The testing period for this analysis was five days.

The COD was determined using the closed reflux colorimetric method according to American Society for Testing and Materials (ASTM) D1252-06.

The Total Dissolved solids (TDS) was determined using the OAKTON TDS meter with sensitivity level of ± 10 mg/l by dipping the probe of the meter into the 500 ml sampling bottle containing spent caustic.

TSS was determined using a portable spectrophotometer with sensitivity level of ± 10 mg/l. The sample was then placed in the cell to measure the TSS value.

RESULTS AND DISCUSSION

Characteristics of Wastewater

In order to ascertain the characteristics of spent caustic at TOR, laboratory analyses were carried out for various parameters. Table 4.1 shows the characteristics of samples of untreated spent caustic, neutralised spent caustic, final effluent of the wastewater and EPA (Ghana) sector-specific effluent quality guidelines for discharge into natural water bodies for oil and gas exploration, production and refining. The table also includes the statistical analysis output of the results obtained.

pH

The average pH of the untreated spent caustic, neutralised spent caustic and the final effluent are 14, 8.16 and 6.88 respectively. The pH of the neutralized caustic and the final effluents were within the EPA Ghana guideline range of 6 – 9 which indicates that the treatment of the sample has been achieved. The Figure 4.1 below shows the plot of sample pH values and EPA Ghana guideline range.

Treatment and Disposal of Spent Caustic at TOR

Table 4.1: Characteristics of Spent Caustic Solution

	Untreated Spent Caustic (USC)		Neutralised Spent Caustic (NC)		Final Effluent (FE)		
Parameter	Average Value	% error $\pm$	Average Value	% error $\pm$	Average Value	%error $\pm$	EPA (Ghana) permissible values
Ph	14.00	0.00	8.16	7.69	6.88	1.94	6 - 9
COD (mg/l)	3,822.01	3.81	632.18	6.55	203.49	4.47	250
BOD ₅ (mg/l)	1,788.36	5.55	598.75	4.45	38.28	7.01	50
Phenol (mg/l)	2.11	28.57	1.67	20.00	0.01	0.00	0.5
H ₂ S (mg/kg)	2,157.36	7.67	731.95	3.13	250.47	5.38	-
RSH (mg/kg)	368.18	7.36	171.91	8.83	21.13	5.18	-
TDS (mg/l)	15.19	3.69	0.43	12.03	0.04	5.18	50
TSS(mg/l)	39.78	5.13	12.33	5.41	6.62	10.53	50

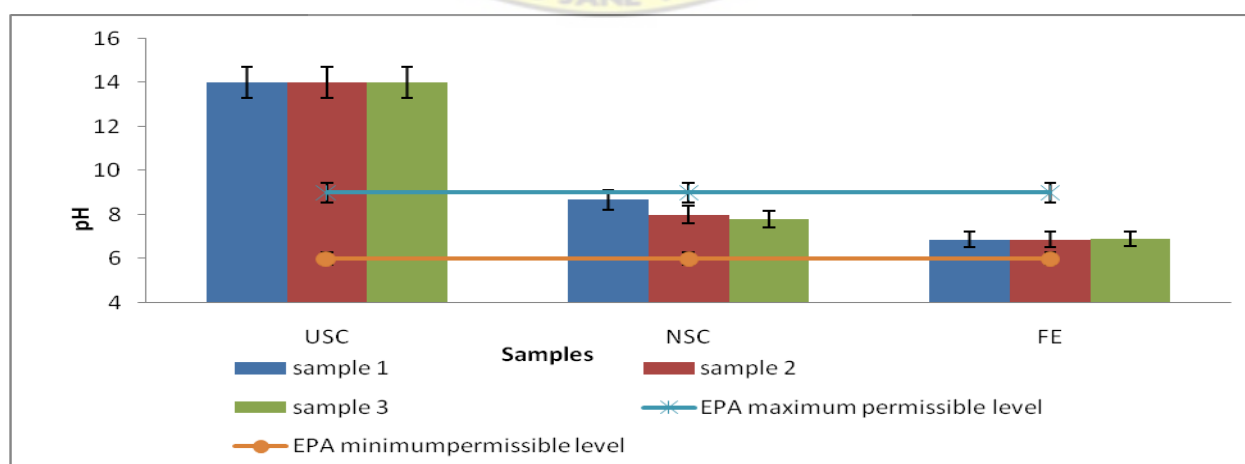


Figure 1: Plot of pH values and EPA (Ghana) guideline

Treatment and Disposal of Spent Caustic at TOR

Biochemical Oxygen Demand (BOD₅)

According to Tchobanoglous *et al* (2003), the BOD₅ / COD ratio of untreated wastewater range from 0.3 to 0.8. A ratio of 0.5 and above means the wastewater can solely be treated by biological means but any value below 0.3 means the wastewater have some toxic components. In the case of this work, the BOD₅ / COD ratio of the final effluent is 0.2 hence the final effluent may contain some traces of toxic substances. Figure 4.2 is the plot of average BOD₅ results of untreated spent caustic, neutralized spent caustic, the final effluent and EPA (Ghana) guideline.

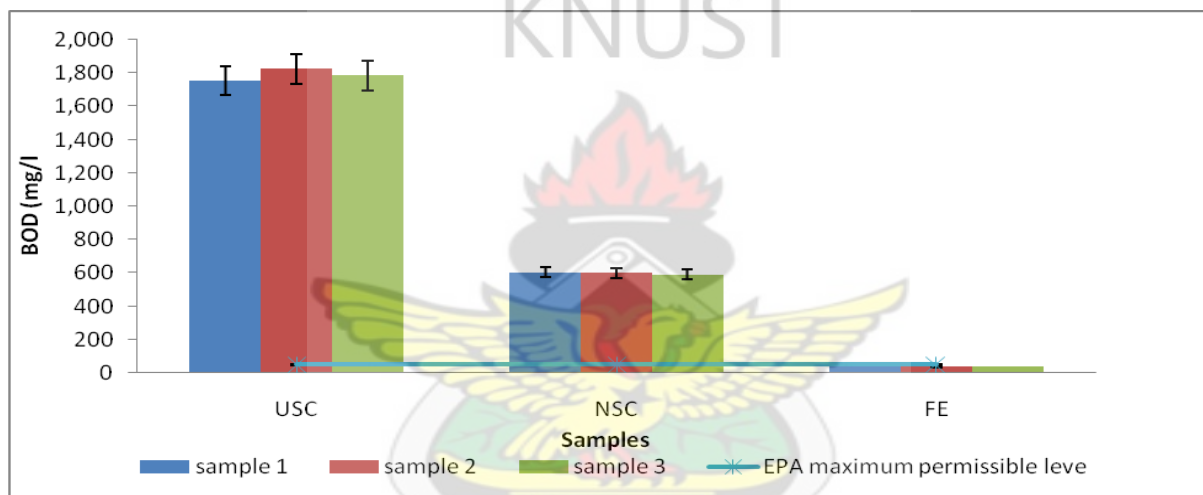


Figure 2: Plot of BOD₅ values and EPA (Ghana) guideline

Chemical Oxygen Demand (COD)

The average percentage reduction of COD after neutralization was 88.47% and after wet air oxidation is 97.60%. The average COD value of the final effluent was below the EPA Ghana guideline of 250 mg/l but that of the untreated spent caustic and neutralized caustic values were greater than the EPA Ghana guideline. Figure 4.3 below shows the plot of the average COD results of untreated spent caustic, neutralized spent caustic and the final effluent compared with EPA Ghana guideline.

Treatment and Disposal of Spent Caustic at TOR

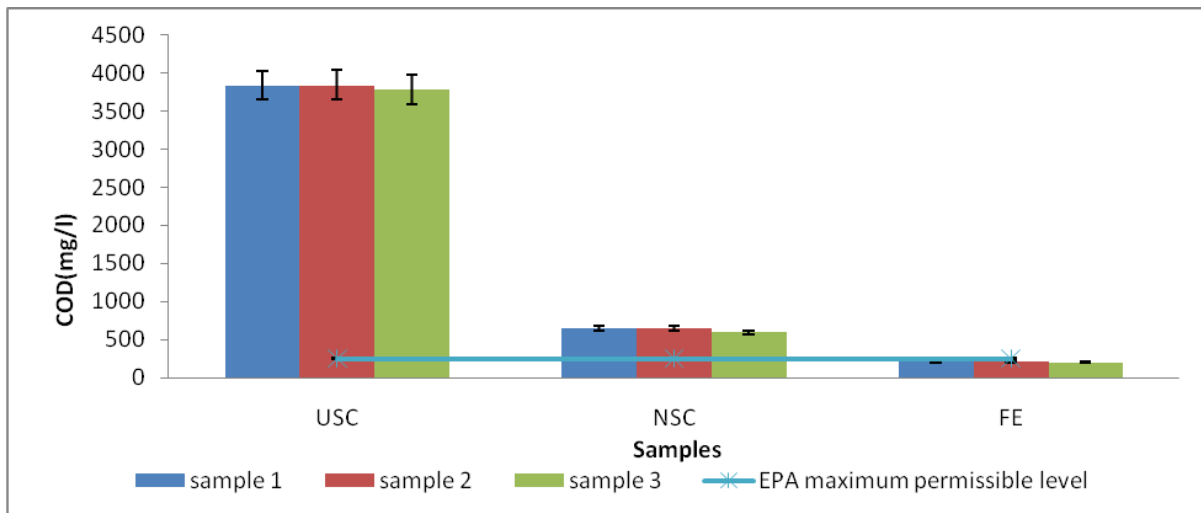


Figure 3: Plot of COD values and EPA (Ghana) guideline

Total Suspended Solids (TSS)

It was well noted that all the average effluent results complied with the EPA (Ghana) permissible guideline of <50 mg/l. Figure 4.4 is a plot of TSS results obtained from field work compared to EPA (Ghana) guideline.

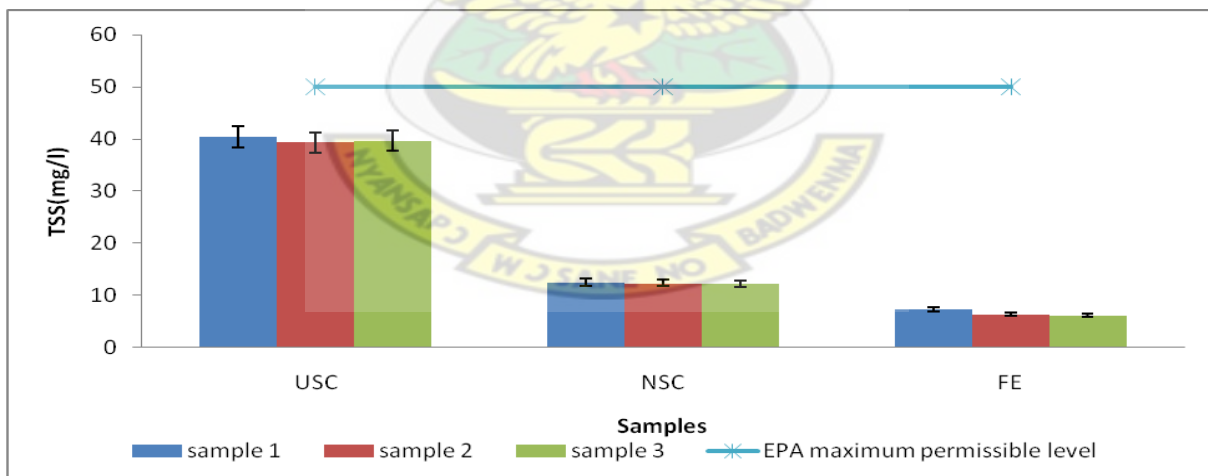


Figure 4: Plot of TSS values and EPA (Ghana) guideline

Phenol

The concentration of phenol in the final effluent was below the EPA (Ghana) guideline of 0.5 mg/l Figure 4.5 shows the plot phenol values from field work and EPA (Ghana) guideline.

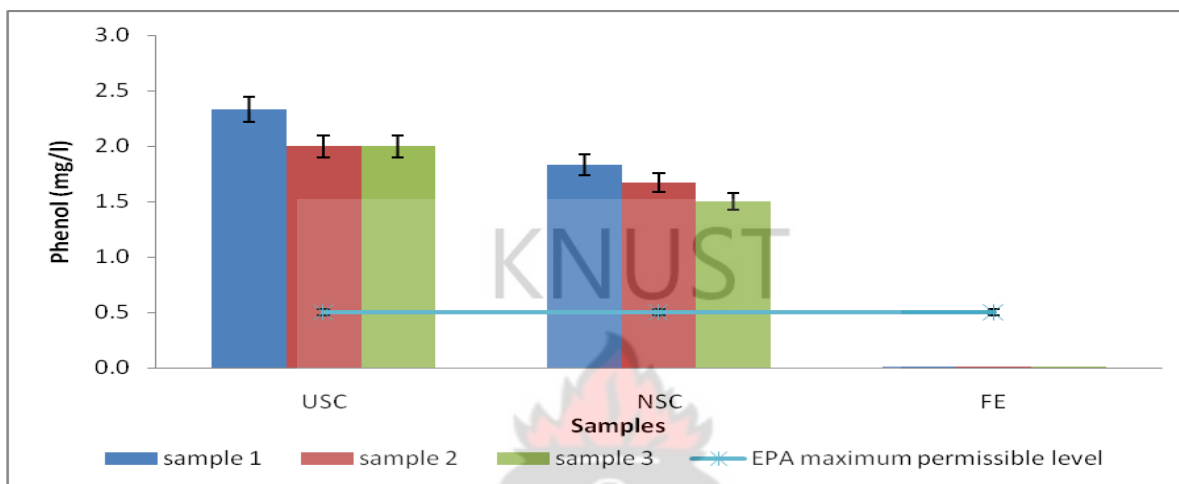


Figure 5: Profile of Phenol values and EPA (Ghana) guideline

Total Dissolved Solids (TDS)

The percentage removal of TDS after neutralization was 76.98% and after wet air oxidation was 92.16%. Figure 4.6 below indicates the plot of sample TDS values and EPA (Ghana) guideline value.

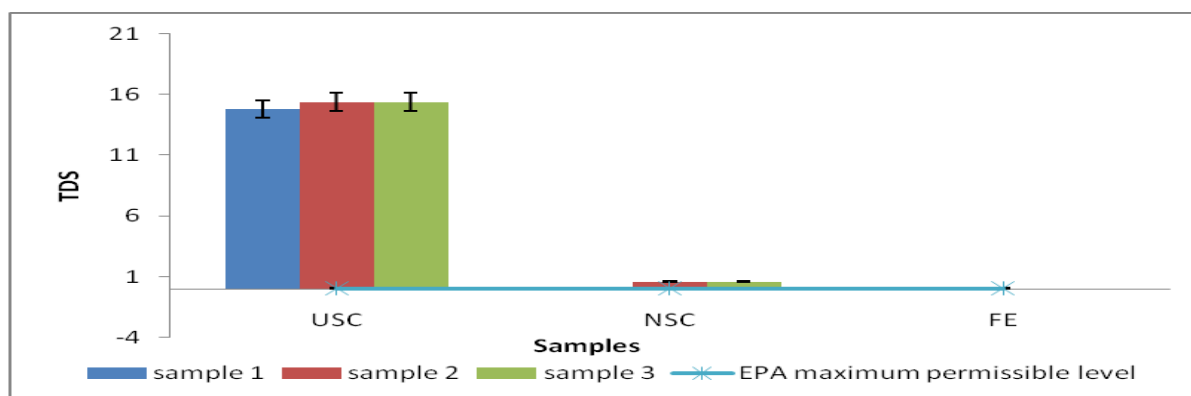


Figure 6: Plot of TDS values and EPA (Ghana) guideline

Treatment and Disposal of Spent Caustic at TOR

Mercaptan (RSH)

The mean mercaptan concentrations in the spent caustic, neutralized spent caustic and final effluent are 368.07 mg/kg, 171.91 mg/kg and 21.13 mg/kg respectively. The mercaptan concentrations reduced by 53.31% after neutralization and 94.26% after wet air oxidation. The Figure 4.7 below is the plot of average RSH values.

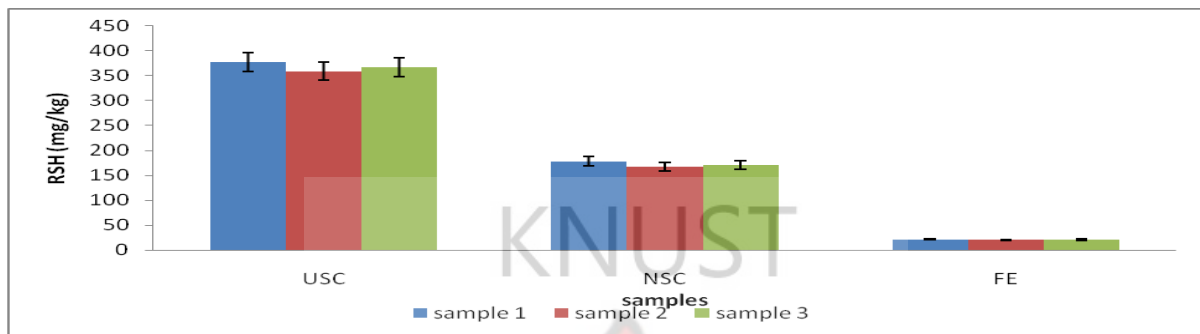


Figure 7: Profile RSH values

Hydrogen Sulphide (H₂S)

There was a general reduction in H₂S concentration during treatment. The mean H₂S values of untreated spent caustic, neutralized spent caustic and final effluent are 2157.37 mg/kg, 731.95 mg/kg and 250.47 mg/kg respectively. The removal percentage after neutralization is 66.07% and after wet air oxidation is 88.39%.

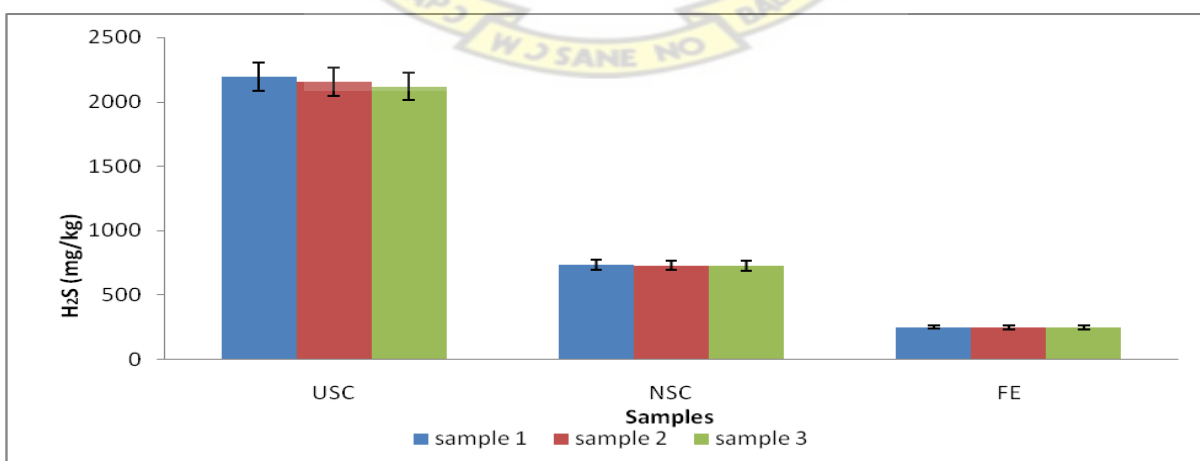


Figure 8: Plot of H₂S values

CONCLUSION

Acid neutralization reduced a majority of the COD. In addition, any sulfides and mercaptans in the spent caustic were released from the spent caustic into the gas phase.

High temperature WAO (240-260 °C) oxidized all reduced sulfur compounds and phenols, eliminate the foaming tendency of the spent caustic, and reduce a majority of the COD producing a biodegradable effluent.

Over the two stage process, 88.46% of hydrogen sulphide (H₂S) was removed while 99.57% of phenol and 94.33% of mercaptans were also removed. Also pH, COD, BOD₅, TDS and TSS values were reduced by 50.93%, 88.97%, 99.03%, 99.73% and 84.37% respectively. The resulting effluent, thus are within the EPA (Ghana) permissible levels.



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