# INDUSTRIAL POLLUTION IN GHANA: SOME SELECTED CASE STUDIES OF INDUSTRIES IN TEMA

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# Dedication

To my husband Nii, my children Richardar, Marguerita, Priscilla (Ranti), Margaret, Richard Ernest(OB) and above all to the Glory of the Living God who has made us to be Winners in all things.

# DECLARATION

It is hereby declared that the thesis is my original work, done under supervision, and has not been presented wholly or partly for another degree in this university or any other university elsewhere.

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# LIST OF ACRONYMS

1. WHO - World Health Organization;
2. AOAC - Official Methods of Association of Official Analytical Chemists ;
3. APHA - The American Public Health Association;
4. TOR - Tema Oil Refinery;
5. TMC - Tuyee Manufacturing Industries;
6. CPC - Cocoa Processing Company;
7. TLC - Tema Lube Oil Company Limited;
8. PFC - Pioneer Food Cannery Limited;
9. BPC - Bridaltrust Paints Company Limited;
10. GTMC - Ghana Textiles Manufacturing Company;
11. GTP - Ghana Textiles Printing Company Limited.

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## Abstract

Waste waters from eight selected industries namely Tema Oil Refinery, Tuyee Manufacturing Industries, Cocoa Processing Company, Tema Lube Oil Company Limited, Pioneer Food Cannery Limited, Bridaltrust Paints Company Limited, Ghana Textiles Manufacturing Company and Ghana Textiles Printing Company Limited were sampled and subjected to various physico-chemical and trace metal analysis to determine levels of pollutants, using standard methods of WHO, AOAC and APHA. Generally, the BOD values were found to be high for all the industries. Some other parameter levels were significantly high enough for the individual industries to deserve attention. Generally, the results seem to suggest that these industries sited in Tema, are likely contributors to the high degree of pollution of the Chemu II and Gao Lagoons which have been reported by various workers as being highly polluted. Consequent to the results obtained, an attempt was made to treat the wastewaters.

Thus wastewaters of three of these major industries Ghana Textiles Manufacturing Company, Pioneer Food Cannery Company Limited and Tema Lube Oil Company Limited, representing the textile, food and petroleum-based industries in the Tema industrial area of Ghana were subjected to various physical and chemical treatments using mainly local materials, to try and reduce the levels of pollutants detected in the earlier investigations. Sedimentation, filtration using paper and sea-sand and adsorption using charcoals prepared from dried coconut husks and palm kernel husks as well as industrially prepared activated charcoal as adsorbents, were some of the physical methods used whilst chemical precipitation and oxidation-reduction were the chemical methods used to bring about the desired results. Six different naturally occurring soil samples from Ankaful, Ekon and Elmina in the Central Region, Asokwa in the Ashanti Region, Bokazo in the

Western Region and Somanya in the Eastern Region were also used to obtain some levels of purification and the results compared.

Most of the methods decreased the levels of pollutants determined in the earlier investigations. Biochemical Oxygen Demand, nitrate, phosphate, conductivity, turbidity and colour of the waste waters were brought significantly to the acceptable limits of World Health Organization and Environmental Protection Agency and trace metals were reduced, in some cases to below detectable limits making the waters safe for re-use domestically and industrially. Sand filtration stood out as the single best method for the treatment of the wastewaters. The easy availability and affordability of sand coupled with the simplicity of its use in filtration should make it a convenient method for the treatment of impure water on a small scale in industry as well as in homes and farmsteads

# CHAPTER ONE

# INTRODUCTION AND LITERATURE REVIEW

## 1.1 POLLUTION

Pollution is as old as civilization and it is one of its surest consequences.[1,2] Among the many environmental problems threatening man today, pollution arouses most interest, because it impacts directly on man through effects on his food supply, health, buildings and other items of cultural heritage as well as overt effects on forests, rivers, coastlines and familiar ecosystems. Pollution, being one of the most serious of all environmental problems, therefore poses a major threat to the health and well being of millions of people and the global ecosystems.[3,4] The effect of pollution is insidious and most of the harmful effects only become apparent after long periods of exposure which most people are not aware of.[5,6] It is therefore imperative that attempts be made to control, if not completely prevent pollution.

It is estimated that presently, there are about $6 \times 10^6$ chemicals that have been introduced into the environment (and these days about 1000 are introduced every year) of which between 66,000 and 95,000 are currently in use commercially.[3] According to Kirkwood and Longley[7], 100,000 chemical substances are in use in Europe today.

According to the FAO, UN and UNESCO, " Environmental pollution is the introduction by man of substances or energy, indirectly or directly into the environment which results in such deleterious effects as harm to living resources and hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water and reduction of amenities."[8] The Royal Commission on Environmental Pollution has another definition for it. To the Commission, "Pollution is the introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structure or amenity; or interference with the legitimate uses of the environment."[7] El-Hinnawi and Hashmi[9] also echo this definition.

Global warming, climatic change and the loss of biodiversity through the extinction of many species may be wholly or partly due to environmental pollution.[3]

The main factors responsible for pollution and other types of environmental deterioration in any community or society may be due to the combined effects of population, affluence and technology.[10] Basically, the larger the population, the greater the extent of environmental deterioration due to related needs for food production, living space, waste disposal, communications and so on. Environmental pressures can therefore increase due to population growth and the expectation of higher living standards.[3] Pollution problems increase in severity when the rate of pollutant emission exceeds the capacity of the environment to assimilate the pollutants. To control pollution therefore, there is a need to look at all these contributory factors carefully to assess their individual contributions and then plan short-term, medium-term and long-term strategies to combat the problem of environmental pollution.

### 1.1.1 TYPES OF POLLUTION

When gaseous, liquid or particulate wastes are introduced into the environment at such a rate that the environment cannot undergo self-purification, then the environment is said to be polluted. Pollution can be classified according to the part of the environment that is affected. Pollutants can be natural or man-made, originating from domestic, agricultural or industrial activities and can end up in the environment, which comprises air, water and land, causing the environmental problems. There is therefore air pollution, land pollution and water pollution.

Land pollution comprises of pollution of soil and the animals and plants (fauna and flora) that inhabit it. The soil is the environment that is usually the first to be polluted by the various types of pollutants.[11]

Water pollution involves all the water bodies like the sea, rivers, lakes and wells, which may be polluted with raw sewage, factory wastes, laundry detergents and insecticide residues from agriculture which are introduced through various activities of man.[5]

Substances that cause pollution and are of natural origin include radioactive fall-out which pollutes the air and can also be introduced into surface and ground waters as well as vegetation. Other substances are minerals, decaying bodies of animals or plants and disease-causing organisms. [6,8]

Man-made pollutants are as varied as the human or anthropogenic activities that produce them.[6,8] Domestic, agricultural and industrial types are usually identified. In rural areas, where sanitary safeguards are lacking, pollution is mostly domestic which is mainly from garbage and excreta[2,6] whilst in urban areas, there are the industrial sources of pollution to contend with, in addition to the domestic source.

Pollution can also be classified as intentional or unintentional. For example, in the quest for increase in food output, a farmer may spray his crop fields with insecticides purposely to kill harmful organisms, but this could also result in pollution, if the chemicals get into the environment. Such pollution is termed unintentional. With regards to intentional pollution, the offender is very much aware of the polluting potential of his actions but all the same goes ahead to do them.

### 1.1.2 EFFECTS OF POLLUTION ON WATER BODIES

The impact of industrial water pollution depends on the specific industry discharges and the assimilative capacity of the water body for the effluents being discharged.[4] The introduction of wastewaters into water bodies may alter their natural state by changing their pH, conductivity, dissolved oxygen,[6] colour[11] and so on, thus, making the water unhealthy. It can also introduce particulate matter and trace metals into the water bodies and can destroy the aesthetic beauty of the water bodies. This interferes with the use of the water for not only domestic purposes but also recreational activities like boating and swimming.

## 1.2 INDUSTRIAL POLLUTION OF THE ENVIRONMENT

With increases in population leading to aggregation into larger communities and the expansion in socialization, human needs also expanded and became more diverse. Subsequently, there arose the need to look for other avenues apart from the natural provisions, to satisfy these needs and this led to the establishment of industries. Industries came to be established to provide goods and services needed for human development and comfort. Crop farming, animal farming, fishing, lumbering, manufacturing and other industries are now well developed to provide man's complex needs.

The varied nature of the products and services provided by the industries requires that they use a diverse array of raw materials and methods in production which give rise to different types of wastes, which have to be disposed of.

With modern civilization, wastes are generated by virtually every manufacturing industrial enterprise. These wastes of industrial origin can be gaseous, liquid or solid. For example, a pharmaceutical industry generates waste solvents when purifying ethical drugs and discarding products or raw materials that do not meet specifications. Large amounts of solid waste is produced in industries like the textile and food industries where remnants of yarn, dye-stuffs and left-over foods are produced in addition to large amounts of hot water that contain other materials.

A wide variety of chemicals and other contaminants, some of which are left-overs of raw materials used in the production, thus form part of the effluents from the modern manufacturing industries.

There is no doubt that at present, the most severe form of pollution in any settlement is the direct result of man's activities.

Here in Ghana, gaseous wastes are mainly produced by industries like Ghana Cement Company Limited(GHACEM), liquid petroleum gas (LPG) filling depots, aluminium production from bauxite, burning of unused fossil fuel during refinery operations and in the production of other manufactured goods whose production processes involve combustion, such as the brick and tile industries.

## 1.2.1 INDUSTRIAL POLLUTION OF WATER BODIES

From the earliest times, humankind has introduced undesirable substances into the very sources from which he obtains water for domestic and other uses as shown by archaeological evidence that the earliest civilizations relied partly on waterways for waste disposal.[1,12] Water bodies had been considered big sinks in which the undesirable materials could be deposited[3] and the waterways were receiving and carrying away the wastes of people living near them.[1,12,13] Thus industries have been generally, conveniently sited near sources of water not only for the reason already stated, but they have been used for the disposal of wastes as well.[3,13] The manufacturing industries sited near sources of water obtain water readily and cheaply for washing, cleaning or cooling in the course of manufacturing various products. Water is also sometimes used to dilute waste products to an acceptable concentration before returning them to the receiving waters.[14]

Liquid wastes can be introduced directly into the water bodies, whilst gaseous ones are dissolved by rainwater which is a powerful solvent or by dry deposition and introduced into water bodies, and through leaching, pollutants from solid wastes can also be introduced into water. No matter the sort of waste produced therefore, the final destination of the waste is the ground and surface waters.

Industries in general use very large quantities of water but very little of it is incorporated into the products, particularly in food and beverage industries. Cooling, washing and steam raising usually account for up to 85% of the total water requirements of industries. Almost all the used water is discharged carrying varying amounts of waste substances[11] such as chemicals.[2]

Loss of water quality of the receiving water bodies may be due to enrichment, that is eutrophication, with degradable organic materials including effluents from the food or other industries, crop farms or fish farms. In addition, the leaching of minerals such as nitrogen compounds, phosphate and potash from agricultural lands or from other sources like agro-based industries can lead to the development of algal blooms in water which can further lead to secondary BOD increases or loads.

Even though industrial effluents disposal, in the form of direct liquid and solid wastes dumping into water bodies[4] as well as indiscriminate hazardous waste disposal is a growing problem for both surface and groundwater pollution, municipal wastes is by and large the largest contributor of the pollutants of water.[4,13] Whilst the municipal wastes are mostly composed of easily decomposable organic materials, industrial wastes can contain highly toxic materials.

According to a study of the sources of industrial pollution made by UNIDO between the coast of La Cote d'Ivoire and Benin, the main producers of industrial pollutants by weight is the textile industry whose wastes contain 30% of all polluting substances, 25% from the food industry, 20% from petroleum industries and about 10% from mineral exploitation and processing. However in Accra, there are seven times more food production factories than textile factories, which are mostly involved in cutting and sewing. In Ghana, there is only one refinery (TOR) and one major petroleum-based industry, Tema Lube Oil Company which are situated in Tema, in the Sakumo II catchment area. Pollution from manufacturing and processing industries are however mainly localized.[2]

Korle, Chemu and Mokwe Lagoons, which are located in industrial areas in Accra, have been reported variously by Amuzu, Biney and GEMS to be highly polluted. The Chemu Lagoon, confirmed as being highly polluted,[15] is located in the industrial zone of Tema Municipal Area and thus is fed with a lot of wastes including liquid wastes in the form of wastewaters from the industries that are situated there.

It is rather unfortunate, that though wastes can be treated to reduce the pollutant levels[6,16] and possibly to retrieve some useful materials from them, even large, well-established industries in Ghana and other countries like Nigeria[2,4] lack the infrastructure for their treatment.

### 1.2.2 IMPORTANCE OF WATER

Living things, including man are composed of cells that contain at least 60% of water[12,13] Apart from water intake to maintain this level, they also use water externally. Organisms can therefore exist and thrive only where there is adequate supply of water. Over 70% of the earth's crust is covered by water, the bulk of which is seawater.[17] Water is our most precious mineral and from the beginning of history, it has been the key to and focus for civilization and development.[12] Water has also been the largest contributory factor in the growth of populations into famous cities. No settlement, whether big or small, can survive without potable water. The need for other necessities like food, clothing and shelter, among others, cannot be met without an adequate supply of water. However, to be suitable for human consumption, water should be substantially free of impurities and bacterial contamination.

### 1.2.3 PURITY OF WATER AND NATURAL PURIFICATION

All waters may show some characteristics of pollution - be it natural or industrial. In many cases, both natural and industrial pollutions are involved, even though the latter is of main concern these days. Seas, rivers, lakes and streams are natural bodies of water that are sources of food and water which are very necessary for the survival of living organisms. These may be altered considerably by 'natural pollution' from sources like radioactive fall-out and biological material decay.

Rivers and streams are more often targets of pollution. Many of the important qualities in which natural rivers differ from one another, such as the type of substratum, amount of silt, oxygen content, acidity, alkalinity, hardness and temperature are just those that are altered by most types of pollution. The main effects of pollution are to some extent transitory, and if they are not too severe, and if the river is long enough and receives enough extra water from tributaries and surface run-off, it can re-purify itself. With the less persistent effects, such as de-oxygenation, suspended solids, or increase in temperature, the alteration may be detectable only for a mile or two below the effluent discharge point. But, usually the pollution is heavier than this and the alterations may persist for a long, long way and a long, long time. Therefore, a conscientious effort has to be made to clean up the environment by man himself since to a very large extent, he put those extra substances where they are not supposed to be.

A river that is made more silty, more acidic, more alkaline, less well-oxygenated, warmer, harder, saltier or richer in nutrient salts is still a natural water as long as the change is not so great as to overstep the boundaries of normal variability. This is true even in the case of some poisons; in spite of the presence of small amounts in the water, it is still considered to be natural water.[5,14] Under natural conditions, flowing waters have powerful self-purifying mechanisms that include sedimentation and biochemical oxidation.[7] Naturally occurring micro-organisms decompose organic wastes and are in turn consumed by larger organisms and fish while aquatic plants in the presence of sunlight, help to restore the oxygen balance, a process that is aided by surface aeration. In most instances of water pollution, the extent is such that the natural purification becomes difficult or impossible. It is therefore necessary to avoid that extent of pollution by treating or cleaning the wastewaters before discharge into the water bodies.

Industrial wastewater effluents affect the purity of the receiving water, in that both soluble and insoluble solid concentrations are increased which affect other parameters like conductivity, pH and so on. Harmful, disease-causing organisms can also be introduced through this channel.

### 1.2.4 WATER POLLUTION AND LIVING ORGANISMS

Pollution of water could lead to contamination of aquatic life and loss of aquatic life, both flora and fauna.[6] For example, some lakes are becoming increasingly polluted resulting in the death of aquatic organisms like fish.[3,7] Pollutants such as trace metals that may accumulate via food webs in terrestrial or aquatic environments, cause toxic effects at the upper trophic levels of food webs to organisms.[7,13] The effects of trace metal pollution at higher trophic levels include delayed embryonic development,[12] malformation and reduced growth of adults of fish, molluscs and crustaceans[18] Some of these metals like Fe, Sn, V, Cr, Co, Mn, Ni, Zn and Cu are essential for metabolism at reasonably low concentrations but in high concentrations, they are toxic to organisms including man.[7,11] They can react with proteins, DNA and RNA affecting metabolic processes and react with other substances causing undesirable physiological changes. They can also cause enzyme inhibition by competing for sites on the substrates and thus change the rate of catalyzed decomposition of metabolites.[18] Some other metals like Pb, Ag and Hg which are normally present in relatively low concentrations in industrial wastewater effluents when ingested by humans and other animals may cause various physiological effects, although some of them may not invoke any response at all. Some of the trace metals like manganese and chromium are also mutagenic and carcinogenic.[5,19] There are also neurological conditions linked to Hg and Pb pollution. In the case of the latter, it is ubiquitous due to its use as an additive in petrol. The effects of pollution may be biological as well as physical. At low concentrations, many heavy metals including Hg, Cd, Pb, As and Cu, inhibit photosynthesis and phytoplankton growth.

In Ghana, the destruction of one-time important lagoons like Chemu and Korle has been attributed to the discharge of untreated wastewaters into the water bodies.[20] Barely thirty years ago, the Korle Lagoon was well-stocked with Tilapia and other useful aquatic organisms and some edible crabs crawled on its banks. Now, the water is without any Tilapia, the edible crabs are gone and the Lagoon has lost its economic value and aesthetic beauty because of pollution.[21] The Korle Lagoon has been reported as being the most polluted coastal lagoon in Ghana.

Water pollution may also arise as a result of increase in concentrations of nutrients. For example, high levels of nitrate are hazardous to health and directly dangerous to infants.[13] Nitrosamines, formed via nitrate and nitrite, are carcinogenic at high concentrations of more than 20 mg/L. Ammonium can also be poisonous as it forms $NH_3$ which is toxic at high pH values[22] and water with a high pH that contains high levels of $NH_4^+$ is toxic to fish.

Discharged wastes may also contain disease-causing micro-organisms which when ingested directly into the body either through food or water can cause diseases like cholera and dysentery and also many intestinal diseases as occurred in the USA and Europe in the nineteenth and twentieth centuries.[7] Water in its non-sterile forms is responsible for 40 % of medical diseases.[23] There is a significant decrease in the production of viable human sperms in technologically advanced countries due to in part exposure to pollutants.[3]

## 1.3 POLLUTION DUE TO MANUFACTURING INDUSTRIES IN GHANA

In Ghana, the manufacturing industries are concentrated in Tema, the industrial city of the country and Accra. However, Takoradi and Kumasi also have a fair share of industries. These industries produce a wide variety of goods, from petroleum-based products such as petrol through cement, textiles, paints to canned foods. Many industries dispose of their wastes, mainly in form of liquid wastes, through their wastewaters, when water is used as a transport medium.[13,17] Although the volumes of wastewaters produced by these industries are low as compared to those of industrialized countries, the unregulated manner of disposal of the wastes constitutes the problem. These wastes are commonly introduced directly without treatment into the water bodies especially surface ones.[4,11,15] In an article captioned "*Water bodies under threat from industrial Pollution'* in the 20th October, 1998 edition of the Daily Graphic,[20] Dr. G. Manful, Director of Operations of the EPA stated that industries in the country discharge nearly 21 million cubic meters of wastewaters into the water bodies.[20]

### 1.3.1 TEXTILE INDUSTRY

The raw materials for the textile industry include cotton yarn, dyestuffs, oxidizing and bleaching agents, silicates, inorganic salts and sodium hydroxide. Textile plants usually have a grey mill for the weaving of cloth and a finishing mill where the cloth is dyed, printed or embroidered. Solid wastes produced in the textile industry are mainly the remnants of yarn and dyestuffs. Large amounts of hot water that contain dissolved and suspended materials, like chloride, sulphate, phosphate and peroxide form the liquid waste. It also contains toxic metals like copper, chromium, zinc, tin and iron and their ions form the liquid waste.

The effluents of the textile industries could also be contaminated with oils, greases and waxes that come mostly from the finishing mill. The dyeing process is the most hazardous, contributing trace metals like Cr, Pb, Zn, and Cu to wastewaters.[24]

### 1.3.2 PETROLEUM INDUSTRY

The main raw material for the petroleum-based industries is petroleum which is a fossil fuel and can contain trace metals like Cd, Co, Ni, Se, B, Bi in addition to nutrients like nitrates, sulphates, nitrites and ammonia.[25] In his book 'Chemical Principles of Environmental Pollution', Alloway[25] stated that fossil fuels contain a wide range of heavy metals and the combustion of these fuels can release Cd, Zn, As, Sb, Se, Ba, Cu, Mn and V in addition to Pb into the environment. Production of petrol, kerosine among other products, is mainly by fractional distillation and since this involves cooling, a lot of hot water is also produced which can increase the temperature of the receiving waters.[6] This hot water can also contain dissolved and suspended solids like sulphur. However, the major pollutants from this industry are gaseous emissions of sulphur, nitrogen and oxides of carbon and hydrocarbons like methane ($CH_4$), ethane $C_2H_6$) which through dissolution can enter into surface and ground waters.[2,9] Particulate materials, aldehydes, $NH_3$ and organic acids can be present too. Other waste substances that are likely to be present in the wastewaters from this industry are oil and grease and organic acids.[4,25]

### 1.3.3 AGRO-BASED INDUSTRY

The raw materials of agro-based industries are diverse and depend on the particular industry involved. They include crops like tomatoes, onions and pepper, farm-reared animals like sheep and goats, fish from inland and coastal waters. From this diverse array of materials, processing is done to obtain a wide variety of manufactured goods. In the agro-based industries, the effluents are mainly organic with some amounts of nutrients like nitrate, orthophosphate and sulphate.[9] Depending upon the particular industry and raw materials used, other pollutants may be present. Although this group of industries is very diverse, all dispose of large amounts of organic wastes creating BOD, suspended solid, turbidity and pH problems.[4,25]

### 1.3.4 WASTE DISPOSAL AND TREATMENT

Archaeological evidence shows that the earliest civilizations relied on at least three strategies to combat the problem of waste accumulation. Firstly, there were centralized rubbish piles that contained diverse wastes including industrial wastes in addition to human waste, secondly by nomadic life maintenance, a system in which population was low and waste disposal was spread over a large area and thirdly waterways were receiving and carrying away the waste of people living near them.[1]

There are currently three main ways of waste disposal; landfill, water-borne disposal with eventual drainage out to the sea and thirdly, dispersal of the waste to the atmosphere.

Solid wastes are used in landfills whilst gases are introduced high into the atmosphere through long chimneys.[16] Industrial wastewaters are commonly introduced into water bodies especially surface ones[4] but can also get into contact with land and vegetation through leaks in gutters and pipelines. As far as land is concerned, the soils have the capacity for adsorbing and filtering off most of the polluting organic, inorganic and trace metals so that the levels are reduced before they leach or permeate into ground water. By and large, the medium that is most affected by industrial wastewaters is surface water.[26]

## 1.4 WATER POLLUTION INDICATORS AND METHODS OF DETERMINATION

Virtually all analytical techniques may have been used for the manual analysis of water,[27] though at present only few find common application. Although there are numerous methods available for the determination of the various parameters to be measured, only a few will be reviewed. The methods that will be discussed include chemical, titrimetric, gravimetric and instrumental methods or combinations of them. The instrumental methods involve those in which instruments are used to directly read off the concentration of the analyte, whilst the chemical ones involve the conversion of the analyte into a new compound usually coloured that can be colorimetrically estimated.

### 1.4.1 PHYSICAL PARAMETERS

The physical parameters considered are temperature, pH, conductivity, dissolved oxygen, suspended solids and dissolved solids. Measurement of the physical parameters has mostly been done by direct reading instruments. Temperature, pH, conductivity, dissolved oxygen and suspended solids can all be measured instrumentally by using mercury-in-glass thermometer, pH meter, conductivity meter and dissolved oxygen meter respectively. Dissolved oxygen can also be determined chemically by the Azide Method that is still very much used.[28] It has also been determined by amperometric titration[29,30] and coulometric titration[31] Suspended solids and dissolved solids have also been determined gravimetrically[32,33] by taking a known volume of the wastewater and filtering it with a 45 μm filter.[34] The method is still very much used for these determinations.

## 1.4.2 CHEMICAL PARAMETERS

The Biochemical Oxygen Demand (BOD) and Chemical oxygen demand (COD) are the chemical parameters discussed. Biochemical Oxygen Demand (BOD) measurement is by the Incubation Method that comes in varied forms. One such method, the Winkler's Azide Modification method involves the use of sodium azide.[32] There is another variation of the Azide method called the Pomeroy-Kirshman-Alsterberg Method[34] in which the weights of NaOH, NaI and $NaN_3$ are different from the Winkler one. There are modifications of the above method in which potassium permanganate and potassium oxalate solutions are used instead of sodium azide.[34] Coulometric titration has also been used to determine BOD.[35]

Chemical oxygen demand can be determined by the dichromate and permanganate methods.[6] After refluxing and cooling, the excess dichromate or permanganate can be determined by titrimetry[32] or colorimetrically. Moore et al[36] and Jirka and Carter[37], in 1949 and 1975 respectively, determined COD colorimetrically after the refluxing with dichromate by reading the absorbance of the resulting solution at 600 nm. COD can be determined by potentiometric titration also.[38]

## 1.4.3 NUTRIENTS

### Orthophosphate

Orthophosphate can be determined by the ammonium molybdate method.[43] This method has a chemical component as well as an instrumental component. The orthophosphate was reacted with vanodomolybdic acid in another method and the absorbance read at 440 nm.[27] Amuzu[39] in 1975, employed a method in which the phosphate was determined colorimetrically. Orthophosphate can also be determined by ion chromatography.

### Nitrate

Nitrate can also be determined by the brucine-sulphanilic acid method[41] that involves colorimetry. The phenol disulphonic acid method is also useful in the determination of nitrate. Kamphake et al[42] and Fishman et al[43] in 1967 and 1964 respectively, determined nitrate by an indirect method involving the reduction of the nitrate to nitrite. Chromotropic acid (4,5-dihydroxy-2,7-naphthalene disulphonic acid) is also used in another method of nitrate determination.[27] Nitrate determination could be by ion chromatography also as was used by Mintah-Boateng in 1995.[44]

## 1.4.4 MAJOR IONS

Potassium, sodium, calcium, magnesium, chloride and sulphate were the major ions measured and hence they are discussed here. Potassium, sodium, calcium and magnesium can all be determined by flame photometry and atomic absorption spectroscopy.[34] Sulphate can be determined by the turbidimetric method as outlined in Official Methods of AOAC.[34] The method involves the precipitation of $BaSO_4$ from the sulphate ions in the wastewaters reaction with $BaCl_2$. Reading of the sulphate concentration was done directly using a spectrophotometer. In another method, $BaCl_2$ was added in excess to the wastewater and the excess precipitated with methylthymol blue.[45] The concentration of the uncomplexed methylthymol blue was read at 460 nm and was proportional to the concentration of sulphate. Amuzu[40] in 1976 determined sulphate indirectly by EDTA titration using Eriochrome Black T as indicator.

Among the methods that can be used for chloride determination, the argentometric method and the mercuric chloride method that are titrimetric are commonly used. Potentiometric titration[46], coulometric titration[46] and conductometric titration[32] which, is very useful in the determination of small quantities of chloride, have been employed. Chloride has also been determined by the displacement of the thiocyanate ion from mercuric thiocyanate complex in the presence of trivalent iron and the absorbance of the resulting solution read at 460 nm.[47]

## 1.4.5 TRACE METALS

Several methods have been used to determine trace metals in all sorts of matrixes.[5] In early studies, gravimetric, volumetric and colorimetric techniques were used. The more common colorimetric methods involve formation of soluble complexes, chelates, with such organic compounds such as dithizone, o-phenanthroline and ammonium pyrolidine dithiocarbamate. For example, iron has been determined by gravimetric, titrimetric and colorimetric methods. Both pyridine and orthophenanthroline have long been used to colorimetrically determine iron (II).[48,49] Potentiometric titration has also been used for metal determination.[50] Modern methods such as anodic stripping voltametry (ASV) and the use of ion-selective electrodes (ISE) based on electrochemical principles are also used.[5]

Other methods of metal determination employ nuclear related techniques. These include proton-induced X-ray emission (PIXE), instrumental nuclear activation analysis (INAA), X-ray fluorescence (XRF) and inductively coupled mass spectroscopy (ICP-MS). Most of these methods are however expensive, and only a few recent studies in Africa[51,52,53] have reported using them.

Practically all metals of interest to the water chemist may be determined by molecular absorption spectroscopy but since the early 1960s, AAS has replaced most of these methods.[54] In Africa by far the most common method for trace metal determination is AAS. The technique is well documented and current publications indicate that it is constantly being improved.[5] The AAS has variety of techniques including flame atomic absorption spectrometry, graphite furnace atomic absorption spectrometry and hydride generation atomic absorption spectroscopy.

The technique involves the conversion of at least a part of the sample into atomic vapour and measuring the absorbance of this vapour at an appropriate wavelength characteristic of the trace metal to be measured.

According to Beer-Lambert's Law,

$$A = \mathrm{Log}\ I_0/I = abc,$$

where A is absorbance, $I_0$ is the intensity of the incident beam, I the intensity of the transmitted beam, a is a constant that is characteristic of the particular system, b is the path length of the optical beam (which can be kept constant) and c is the concentration of the analyte. The absorbance is directly proportional to the concentration of the analyte in the sample. By comparing the absorbance with those obtained for reference samples of known concentrations under the same experimental conditions, the analyte's concentration is evaluated.

The AAS is generally composed of a light source of a hollow cathode lamp (HCL), an atomizer, a monochromator, a photoelectric detector and a signal processor. Samples analyzed are usually in solution that is sprayed into the flame. For good and reliable results, the absorption should be between 20 % and 80 %, corresponding to absorbance of 0.10 and 0.70 respectively. Presently, the trend is towards the analysis of solid samples[55] which allows for the circumvention of processes that otherwise would have introduced contamination which processes include dissolution and dilution.[5] Electrothermal AAS, one of the most attractive methods for determining trace elements in biological samples, involves the use of the solid sampling technique.

The techniques of AAS are subject to various interferences. When concomitant elements affect an alternation in those physical and chemical properties or processes that control the final population of neutral ground state atoms of the sample in the absorption cell, interference with the analytical signal results. The various innovations of the AAS are Hydride GAAS which is employed in the analysis of elements that form volatile hydrides, that is, Hg, As, Se, Sb, Sn and others.[56] Analyte is simultaneously converted into its hydride by using sodium borohydride ($NaBH_4$) or tin (II) chloride as reducing agent and separated from its matrix.

In spite of the numerous setbacks of AAS, some of which have been enumerated above, it has advantages over other methods. These include high sensitivity for a wide range of metals, including those that are difficult to determine by flame photometry and its specificity. Also, the method is fast and only a small amount of the sample is needed. Also, any metal can be determined in the presence of other metals and there are very few metals that cannot be so determined. Some of the metals that can be measured are Groups $1^A$ and $1^B$, Cd, Cr, Cu, Fe, Pb, Mn, Ag and Zn.[34]

Other methods that have been used for the trace metal determination are atomic emission spectroscopy, X-ray fluorescence, neutron activation analysis, differential pulse polarography, anodic stripping voltametry and isotope dilution mass spectrometry. All of the above methods have detection limits in the nanogram range.[57] However, in this study, the flame atomic absorption spectroscopy was used. Inductively coupled plasma emission spectroscopy is rapidly becoming one of the most important techniques of trace metal analysis. One distinct advantage of this method over atomic absorption is its capability of multi-element analysis and the linearity of its calibration curve over at least five orders of magnitude compared to two magnitudes for AAS.[5]

Even though there are varied methods for the determinations, the choice of methods was primarily based on the availability of the chemicals, instruments and other logistics.

## 1.5 TREATMENT OF INDUSTRIAL EFFLUENTS

In the olden days, when population and the level of human activities was low, not much water was used and hence no-one cared about pure or impure water or purification of water because nature did the purification on its own and that was enough. Nowadays, with an increase in population and a high demand for potable water, the natural purification alone is inadequate so there is a need to treat the wastewaters before discharging them into the water bodies.

Before a wastewater can be treated successfully, the pollutants and their levels in the waste should be known[19] and the nature of the wastewater, whether the pollutants are dissolved, colloidal or suspended and whether the pollutants are organic or inorganic,[13] so that the type of treatment the waste is subjected to, is related to the pollutants present otherwise, a lot of resources will be wasted on treatment without achieving any good results.

The treatment of wastewaters is usually in three stages classified as primary, secondary or tertiary.[17,58]

## 1.5.1 PRIMARY TREATMENT

This is physical[3,58] and can also be referred to as mechanical.[13] The physical methods include phase separation which consists of filtration and sedimentation and phase transfer which involves adsorption. Filtration and settling of wastes remove larger particles by filtering through large screens and settling in ponds or lagoons. Water is removed from the top of the pond and released. Water thus treated, has no sand or grit but still carries a heavy load of dissolved organic matter, dissolved salts, bacteria and other micro-organisms.[58] The organisms use the organic material for food and as long as there is sufficient oxygen, they will continue to grow and reproduce. If the receiving body of water is large or long enough and the organisms have enough time, the organic matter will be completely degraded.[6]

### 1.5.2 SECONDARY TREATMENT

This is mostly biological and usually follows the physical or primary method.[17,58] During anaerobic treatment, organic substances are broken down in the absence of oxygen to water, carbon dioxide and organic gases such as methane by micro-organisms.[3,6,13] In the presence and with addition of oxygen, the products are mainly water and carbon dioxide. With other organic substances such as fats, starches, proteins, amino acids, alcohols, cellulose and other substances of varying degree of complexity, they are converted into ammonia ($NH_3$), nitrate ($NO_3$-N), phosphate ($PO_4$-P), sulphate ($SO_4$) and carbon dioxide ($CO_2$) consuming large amounts of oxygen.[9] The wastewater is held until the organic material has been degraded by bacteria and other micro-organisms. To encourage this action, the wastewater is mixed with large quantities of highly oxygenated water or the water is aerated directly as in the trickling filter system. In this process, the water is sprayed over the surface of a column of rocks and stones to increase the amount of dissolved oxygen. The rock also provides a place for the bacteria and other microbes to attach so that they are exposed simultaneously to the organic matter and oxygen. These micro-organisms feed on the dissolved organic matter and small suspended particles which then become incorporated into their bodies as part of the cell structure.[13] The bodies being larger than the dissolved organic and suspended matter, concentrate the organic wastes into particles that are large enough to settle out. The sludge that settles therefore consists of living and dead micro-organisms and their waste products.

Another method, the activated sludge treatment involves some of the sludge being returned to the aeration tanks, to be mixed with incoming wastewater. Like the trickling filter method, both produce sludge that settles out of water. The remaining sludge is concentrated and often dried before disposal. The disposal could be carried out in landfills, but some can be composted and returned to the land as fertilizer if not toxic. After complete oxygenation, heterophytic aerobic bacteria are replaced by anaerobic bacteria which can produce methane, hydrogen sulphide, ammonia ($NH_3$) and iron (II) sulphide (FeS)[9] When wastewaters contain high levels of organic solids, these can settle creating conditions that are highly offensive to the eye and the nose. This is the first stage in the natural rectification or purification process.

The primary and secondary treatments are common in N. American countries. The water discharged from these sewage treatment plants must be disinfected using the least costly method with chlorine or using ultrasonic energy to mechanically break down waste. The latter is less harmful and more effective but more expensive than chlorination.[17]

### 1.5.3 TERTIARY TREATMENT

This involves a variety of different techniques to remove dissolved pollutants left after the primary and secondary treatments.[17] The chemical ones include acid-base neutralization, chemical precipitation and oxidation and reduction.[3] These remove phosphorus and nitrogen, elements that increase aquatic plant growth. It is very costly because it requires specific chemical treatments of the wastewater to remove specific problematic materials. For example, hydroxyl ions ($OH^-$) are used to reduce or remove cations like Fe (II), Fe (III), Al (III). Hence, as far as tertiary treatment is concerned, industries have to maintain their own tertiary treatment facilities because of the specific nature of their waste products.[17]

The mechanical method removes settleable solids. It normally reduces the organic component of the sewage by 30 %. This results by the phosphate present chemically combining with the suspended solids which when removed results in a decrease of the amount of phosphates.[13] The biological methods involve the use of micro-organisms to decompose and break down the organic pollutants under aerobic and anaerobic conditions. This decomposition process is extremely complex and consists of a long series of sub-reactions with the process rate depending on many factors such as the oxygen content (DO), pH, temperature, type of pollutants, the presence of toxic substances, method of treatment and particle size.

## 1.6 WORK DONE ON INDUSTRIAL POLLUTION IN GHANA

Some amount of work has been done on the quality of wastewaters from manufacturing industries but very little work has been done on treatment of the wastewaters.

Mintah-Boateng[44] (1995) of Water Resources Research Institute (now Water Research Institute) of Council for Scientific and Industrial Research (CSIR) determined the quality of wastes including wastewaters from selected industries among which were Tema Oil Refinery and Unilever. Biney[59] (1991) also worked on industrial effluents and found the wastewaters to have polluting potential. Amekor[60] of the EPA did work on the quality of water in the Chemu Lagoon in 1995 in which he determined the level of pollutants in some selected industries including Tema Oil Refinery, Ghana Textiles Printing, Tema Textiles Limited (now Ghana Textiles Manufacturing Co.), Unilever and Bridaltrust Paints. He also concluded that the effluents were quite polluting and had serious effects on the Chemu and Gao Lagoons. Bruce-Tagoe[21] in 1996 worked on wastewaters from some selected industries in Accra, which empty their wastewaters into the Odaw River and Korle Lagoon. The study showed that the industries are potential contributors to the pollution of these water bodies.

In all the industries investigated by Bruce-Tagoe, only Ghana Industrial Holding Company (GIHOC) Pharmaceuticals treat their wastewaters to some extent. Biologically, the wastewater is aerated first and then chemically, alum is added to it. To a large extent, the treatment is successful, reducing most of the parameters including BOD, COD and dissolved solids. In 1997, Togbe and Co.[61] in the University of Ghana worked on the effluents of Pepsi and Coca Cola companies which bottle soft drinks and are sugar-based industries and established that they are potentially polluting in BOD.

Presently, Acheampong[62] of Ghana Standards Board and some other workers of the EPA are monitoring the effluent quality of wastewaters of selected industries in the industrial zone of the Tema Municipality.

## 1.7 OBJECTIVE OF PRESENT WORK

There is very little quantitative information on the extent of industrial pollution in Ghana, but what information is available point to the fact that, there is a growing problem that threatens the life, health and well-being of particularly the workers in the industries and the whole nation. This is particularly so, taking into consideration the fact that facilities for the treatment and disposal of industrial wastewaters are rudimentary or non-existent.[2] Very few industries make an attempt to treat or dispose of their wastes properly. This is gradually endangering the life of man, but in his quest for a better and more fulfilling life, he is constantly exploiting whatever materials are available to manufacture what he needs. It is unfortunate that though wastes can be treated to reduce pollutant levels, even large, well established industries have little or no infrastructure for the treatment of their wastes, especially liquid wastes and dump them directly into the environment without any prior treatment. The wastes can be processed to recover useful materials or treated to reduce their volume, toxicity, or mobility thus reducing their impact on human health and the environment.[16] To ensure the effective treatment of wastewaters, the level of treatment should be related to the degree of pollution expected in the wastewater source and the nature of the wastewater, whether the pollutants are dissolved, colloidal or suspended and whether the pollutants are organic or inorganic.[6] Hence, there is a need for information of pollutant levels in wastewaters before an attempt is made to treat them.

Treatment of wastes is very costly and impacts negatively on the profits of industries and that is one reason most are reluctant to treat their wastes and simply release them into the environment. In a World Bank Report on Nigeria, water pollution was reported as having the second highest potential for future negative impact on the GDP of Nigeria, a developing country, and this was estimated at US$1 billion annually that can also put 40 million people at risk.[4] This could well be repeated for Ghana, another developing country but may be, not in the same proportions.

Great conservation problems face humankind today with regards to the keeping of water bodies clean and maintaining adequate and qualitatively useful supplies of this natural resource[22] in view of the rapid growth of population and the daily rise in the demand for water. *The International Environmental Technology* edition of Nov./Dec. 1998, referred to a press release in which water was referred to as the most important raw material of the 21st century. It also pointed out that an attempt must be made to ensure that water sources remain unpolluted or is purified since this is a world-wide problem. Pitt[53] reported that a third of the world's population lives in seriously water-short regions, mostly in developing countries. Within this group, 1.2 billion people do not have access to clean water. He also predicted that within the next decade, another 1 billion may fall into this water-deficient category, if measures are not taken to reverse the trend.

The costs of the effects of pollution are the depreciation of resources, lost productivity and the increasing resources used in cleaning up or improving polluted environments including water. These are high and are increasingly occupying the attention of governments and politicians in technologically advanced countries[3] as well as in developing countries like Ghana and Nigeria.[2,4,25]

Quick and inexpensive ways of treating the wastewaters are therefore necessary to make treatment of wastes attractive and less cumbersome to people, especially those in industry so that they can treat their wastewaters before dumping them in the environment or before reusing them for potable purposes. There is need now than ever before for the treatment of wastes especially liquid wastes, in one way or the other before they are disposed off finally into the environment.

In the present study, the industries were put into three groups, the textiles, food or agro-based and petroleum-based industries. To be able to do a good job on them, it is imperative that the raw materials they use, the methods of production and other vital information be obtained so that the problem can be tackled right from its inception, since industrial pollution has the notorious property of being cumulative and finally, producing disastrous effects that are either irreversible or expensive to abate.[11]

To make wastewater treatment easier and cheaper will therefore be a very welcome and preferred thing indeed, since it will help industries to maximize their profits whilst also safeguarding the health of the people and the environment at large. It is towards this end that this study was initiated to:

a) determine the quality of various wastewaters from selected industries to ascertain the major pollutants and their levels;

b) identify those industries that need to clean up or treat their wastewaters before their discharge into the receiving water bodies;

c) investigate and find out other alternate and cheaper methods for wastewater treatment using local materials.

# CHAPTER TWO

# METHODOLOGY

## 2.1 SAMPLING OF WASTEWATERS

### 2.1.1 INDUSTRIES SAMPLED

Requests to sample the wastewater effluents were sent to thirty industrial companies but only nine industries responded favourably. Eight of them were sampled, because although Unilever (Ghana) Limited responded favourably, permission could not be obtained for the sampling to be done despite several visits to the factory. The industries sampled are all sited in the Light and the Heavy Industrial Areas of Tema. Their products and the nature of their wastewaters are shown in Table 1.

## TABLE 1 INDUSTRIES, PRODUCTS AND CATEGORY OF WASTEWATER

| INDUSTRY | ACRONYM / NUMBER | PRODUCTS | CATEGORY OF POLLUTANTS |
|---|---|---|---|
| Tema Oil Refinery | TOR<br>1 | petrol, kerosine, liquid petroleum gas (LPG). | organic, colloidal and highly saline. |
| Tuyee Manufacturing Co. | TMC<br>2 | industrial starch, writing chalk, cement. | organic waste, dense and colloidal. |
| Cocoa Processing Co Ltd. | CPC<br>3 | Cocoa powder, chocolate, cocoa butter. | slightly, viscous colloidal. |
| Tema Lube Oil Co. Ltd. | TLO / TLC<br>4 | petrol and diesel engine, hydraulic and gear oils, lubricating oils. | organic waste, colloidal. |
| Pioneer Food Cannery Co. Ltd. | PFC<br>5 | canned fish. | pinkish and colloidal. |
| Bridaltrust Paints Manufacturing Co. | BPMC<br>6 | oil and emulsion paints. | coloured, densely colloidal suspension. |
| Ghana Textile Manufacturing Co. | GTMC<br>7 | printed textile materials. | coloured colloidal suspension. |
| Ghana Textile Printing Co. Ltd | GTP<br>8 | printed textile materials. | coloured colloidal suspension. |

### 2.1.2 THE CHOICE OF PARAMETERS

Parameters determined were limited by availability of equipment and reagents, but as much as possible it was done in such a way as to allow comprehensive, logical and coherent conclusions to be made. Parameters determined were:

a. **Physical** - Temperature, pH, conductivity, dissolved oxygen, suspended solids, dissolved solid;
b. **Chemical** - Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD);
c. **Nutrients** - orthophosphate, nitrate;
d. **Major ions** - sodium, potassium, calcium, magnesium, sulphate;
c. **Trace metals** - Cu, Pb, Co, Zn, Al, Mn, Ni, Cr and Fe.

### 2.1.3 SAMPLE COLLECTION AND PRE-TREATMENT

At each factory, the sampling was done at the end of the production line, as the wastewaters issued out into the drains that carry them into the Chemu Lagoon and appropriately labeled. At Tema Oil Refinery, a sample was collected from the Premier former cooling water observation point and labeled TOR$^{A}$. Oily petroleum fractions contained in this wastewater has been skimmed off by a mechanical process, after which the wastewater issued out into either the API or the Chemu Lagoon. At the API, by another mechanical device, an attempt is made to skim the oil off the top. The skimmed oily top that goes into the API was sampled and labeled TOR$^{B}$. When this oily wastewater had been passed through the API, it was collected and labeled TOR$^{C}$.

## Cleaning of Sample Container

High density polythene containers were used because they suffer less from evaporation and adsorption-ion exchange problems.[5] They are also less expensive and less fragile. The containers with well-fitting stoppers were pre-treated by washing with acetone to get rid of organic substances, washing with detergent, rinsing with deionized water and steeping in 1.6 M nitric acid solution for between forty-eight hours to seventy-two hours.[5] The containers were finally rinsed with de-ionized water and drained before use for holding the samples. Replicate samples were taken for each industry at every sampling.

Attempts were made to sample at two weeks intervals but sometimes it was impossible to do so because personnel who should have accompanied the worker to the sampling points because of security reasons were not available. Each industry was sampled at least on five different occasions. One Liter volume of each sample was taken. In order to avoid contact with air, which was necessary because pH and conductivity were to be determined, the sample containers were completely filled with the wastewaters.[5,27] The wastewaters were collected into the pre-treated plastic bottles. Separate samples were collected for the field and laboratory measurements. Temperature, pH, conductivity and dissolved oxygen were determined at the sites immediately after sampling. The samples for other determinations were transported to the Water Quality Laboratory of the Water Research Institute in ice-chest and kept under a temperature of 4 $^0$C and in the dark to prevent biological activity until they were needed for the remaining analysis.[5] A third sample collected for metal determination, was acidified at the time of collection by adding 2.0 mL of conc. nitric acid per liter of sample to reduce the pH to less than 2.[32] For most trace metals like Fe, Cu, Ni, Al and Zn, this ensures stability for several weeks. Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) were determined within four and twenty-four hours after collection of samples respectively.[32]

## 2.2 DETERMINATION OF PARAMETERS

All the determinations of the level of pollutants were done by Standard Methods of World Health Organization (WHO), the American Public Health Association (APHA)[32] and Official Methods of the Association of Official Analytical Chemists (AOAC)[34] at the Water Resources Research Institute (CSIR). In the determination of orthophosphate and trace metals standard solutions were used for plotting standardization curves. Treatment methods employed were as suggested by Hynes[3], Alloway[6] and Kemi[13].

### 2.2.1 PHYSICAL PARAMETERS

Temperature, pH and conductivity were determined using a mercury-in-glass thermometer, a Gallenkamp pH meter with glass combination electrode and an Orion 120 conductivity meter respectively, on the field immediately after sample collection. Buffer solutions of pH 4.0 and 10.0 provided by the manufacturer were measured with the pH meter before the actual measurements with the wastewaters were done. The conductivity meter was also used to measure standard solutions of potassium chloride (KCl) before its use to measure the conductivity of the wastewaters.

Total suspended solids was determined by a gravimetric method. 50.0 mL portions of the sample were filtered through pre-dried and pre-weighed 0.45 μm millipore Watman filter papers. The filters with residues were dried in the oven to constant weight at 103 °C overnight and weighed again after cooling in a desiccator.

The determination of total solids (TS) was done by taking 20.0 to 100 mL volumes of the wastewaters in already weighed dry porcelain or glass dishes and heated over a water-bath until all the solvent water had evaporated. The dishes were then transferred to the oven and heated at a temperature of 103 $^0$C overnight to dryness. The dishes and their contents were then cooled in a dessicator and then weighed again.

In the determination of total dissolved solids, samples of the wastewaters were filtered through 0.45 μm millipore filter and measured volumes of either 50 or 100 mL of the filtrates taken in already weighed dry porcelain or glass dishes and heated over a water-bath until quite dry. The dishes with the residues were further dried in an oven at 103 $^0$C overnight until a constant weight was obtained.

## 2.2.2 CHEMICAL PARAMETERS

### Dissolved Oxygen

The narrow-necked, 300 mL BOD bottle was slowly and carefully filled with the wastewater sample to avoid trapping air bubbles. 2.0 mL each of manganese (II) sulphate and alkaline-azide-iodide solutions were added below the surface. The bottle was stoppered and inverted several times to mix the contents very well. The preparation of the alkaline-azide-iodide solution is outlined in Appendix IV. A floc of manganese hydroxides of higher oxidation states was formed, which was allowed to settle. 2.0 mL of conc. $H_2SO_4$ was then added down the neck of the bottle. The contents were mixed by inversion until iodine ($I_2$) formed through a redox reaction between the manganese and iodide ions was uniformly distributed. 100.0 mL portions of the iodine solution were titrated immediately with a standard sodium thiosulphate solution using a starch indicator. The soultion was titrated with the thiosulphate solution until pale yellow before the starch solution was added.

## Biochemical Oxygen Demand

The determination of biochemical oxygen demand was by Winkler's Azide Modification Method. Two BOD bottles were filled with 250.0 mL of samples. To one was added 2.0 mL of manganese (II) sulphate solution and 2.0 mL alkaline-azide-iodide solution prepared by dissolving specific weights of NaOH, NaI and Na azide as outlined in Appendix IV, was also added below the surface of the wastewater. The bottle was stoppered, shaken well and allowed to stand. Flocs of manganese hydroxides of higher oxidation states were formed. When the precipitates were about to settle, the bottle was shaken again. After the flocs have settled, 2.0 mL of conc. $H_2SO_4$ was added down the neck of the bottle. The contents were mixed by inversion until iodine formed was uniformly distributed. The dissolved oxygen (DO) was determined as above. The other bottle containing only wastewater sample was incubated at 20 °C for five days and thereafter the DO was determined. A blank determination was done using dilution water, prepared as in Appendix IV instead of the sample but treated in the same way as the incubated bottle.

### Equations of the Reactions Involved in Precipitation

1. $Mn^{2+} + OH^- \longrightarrow Mn(OH)_2 + O_2 \text{ (from sample)} \longrightarrow Mn(OH)_4$ etc.

2. $Mn(OH)_4 + H^+ + I^- \longrightarrow I_2 + \text{Lower Hydroxides} + H_2O$

### Equations of the Reaction Involved in Titrimetry

$$I_2 + S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

## Chemical Oxygen Demand

The chemical oxygen demand was determined using the dichromate reflux method. 10.0 mL of the sample, 1.0 mL of $Hg_2SO_4$ (aq), 5.0 mL of standard $K_2Cr_2O_7$, 15.0 mL $Ag_2SO_4$ in $H_2SO_4$ were put together and refluxed for 2 hours. After reflux, the contents of the flask were cooled, diluted with de-ionized water to 50.0 mL and titrated with standard ferrous ammonium sulphate solution using ferroin, an o-phenanthroline ferrous complex as indicator. The silver sulphate, $Ag_2SO_4$ acts as catalyst, whilst $Hg_2SO_4$ prevents chloride interference. After reflux, excess dichromate was titrated against standard ferrous ammonium sulphate and the COD measured as oxygen equivalent, proportional to the dichromate consumed during the reduction by the organic matter. The chemically oxidizable substances in the sample reduce $Cr^{6+}$ ions in $K_2Cr_2O_7$ to $Cr^{+3}$.

**Equations of the Reaction Involved In Titrimetry**

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$$

### 2.2.3 NUTRIENTS

### Nitrate

Nitrate was determined by the brucine-suphanilic acid spectrophotometric method. The nitrate in the wastewaters reacts with brucine in $H_2SO_4$ at 100 $^0$C to form a yellowish - orange coloured substance, the absorbance of which was measured at a wavelength of 410 nm. 10 mL of wastewater was pipeted into hard-glass test tubes. To each of these tubes was added 2 mL of 30% NaCl solution. Tubes were swirled and placed in 1-10$^0$ C water-bath and 10 mL of 7.5 M $H_2SO_4$ was pipetted into each tube and swirled. All the tubes were allowed to stand to come to thermal equilibrium with the environment. Finally, 0.5 mL of the brucine reagent was added to each tube. An extra tube that had the wastewater sample and all other reagents except brucine was added for colour control. The tubes were all swirled again and placed in a boiling water bath for exactly 25 min at 95 $^0$C. The tubes were then transferred to a cold water bath and allowed to cool to between 20 °C and 25 °C. The outside of the tubes was dried and the absorbance of their contents read against the reagent blank at 410 nm.

A set of standard solutions was prepared containing 0.1 - 2.0 mg of $NO_3$-N using analytical grade $KNO_3$ per liter which, was also treated in the same way as the wastewaters. Calibration curves were plotted of concentration in mg/L against absorbance and the gradient calculated as shown on Fig. 40. The value of the gradient was multiplied with the individual absorbance of each sample to calculate their nitrate concentration or the concentrations were just read off the graph.[32]

### Phosphate

The phospho-molybdate method[35] was used in the determination of orthophosphate. 100 mL of wastewater and 100 mL of a 0.50 mg/L standard phosphate solution were measured into separate conical flasks. To the contents of each conical flask was added 4.0 mL of ammonium molybdate solution. After thorough mixing, 0.5 mL of stannous chloride solution was added and mixed to produce a blue colour. Absorbance was read at 690 nm within 5 to 10 min, after the spectrophotometer had been calibrated using the standard phosphate solution. A calibration curve was plotted using 0.1 mg – 0.5 mg/mL of $PO_4$-P.

## 2.2.4 MAJOR IONS

### Sodium and Potassium

The samples were first filtered through a 45 μm millipore filter membrane and the Na and K determinations done photometrically using a Gallenkamp Digital Flame Analyzer. Sodium and potassium were measured at 589 nm and 768 nm respectively, using propane air as fuel-oxidant, after measurements of the concentrations of standard solutions of potassium and sodium nitrates.

### Calcium

Calcium was measured by EDTA (ethylenediaminetetraacetic acid) complexometric titration using a murexide (ammonium purpurate) solid as indicator.[35] The preparation of the EDTA solution is described in Appendix IV. 100.0 mL of the sample was measured into a conical flask and 2.0 mL of 1 M NaOH solution added. A pinch of murexide solid was added. The resulting dark red solution was titrated with EDTA solution until a purple color was obtained. This is the end point of the titration. From the results calcium concentration and calcium hardness of the wastewaters were calculated.[32]

### Magnesium

In order to obtain magnesium concentration, total hardness of each wastewater was first determined. The total hardness was determined using EDTA[32] which forms complexes with certain ions. 50 mL of the sample was measured into a conical flask and 1.0 mL of ammonia buffer and a pinch of Eriochrome Black T solid was added. The resulting wine coloured solution was titrated with standard EDTA solution until an end point of sea-blue colour was obtained at a pH of 10. The total hardness was calculated from the results obtained.[32] Calcium hardness was subtracted from the total hardness to obtain magnesium hardness and finally magnesium concentration since it is generally believed that the hardness of water is due to the presence of calcium (Ca) and magnesium (Mg) ions.[32]

### Sulphate

The determination of sulphate was by the turbidimetric method.. 5.0 mL of conditioning reagent was pipeted into 100 mL portions of samples in 250 mL Erlenmeyer. The contents of the flask were mixed on a magnetic stirrer. While stirring, a spoonful of $BaCl_2$ solid was added and then timed. A white precipitate of $BaSO_4$ of uniform size was formed. Stirring was done at constant speed for exactly 1 minute and some of the solution was transferred immediately into a cell and the turbidity was measured at 30 sec. intervals for 4 minutes and the maximum reading recorded. A Philips UV/VIS Spectrophotometer was used to measure the sulphate at a wavelength of 420 nm. A blank determination using de-ionized without $BaCl_2$ was subtracted from each reading. A standard curve was prepared by using serially diluted samples of 0 – 40 mg/l $SO_4$ in 5 mg increments and the concentrations read off.

### Chloride

The determination of chloride was by Mohr's method. 100 mL each of the wastewater and of de-ionized water were measured into separate conical flasks and 1.0 mL of potassium chromate added to each. The resulting solutions were titrated against standard aqueous silver nitrate solution until the first permanent reddish-brown color was obtained at the end point. The de-ionized water was used as a blank to determine the amount of chloride in de-ionized water for use in cases where there was dilution.

## 2.2.5 TRACE METALS

As already stated, on collection of the samples in pre-treated plastic bottles, they were acidified with concentrated nitric acid to a pH of about 2 and kept refrigerated until analyzed. Since the samples were colloidal in nature, wet digestion was done with nitric acid in a digester (Teflon bomb) for 8 hrs at $160^0$ C to make them clear and colourless for total metal estimation.[5,64] For dissolved metal estimation, the sample was acidified immediately after sampling with $HNO_3$ and then filtered using 45 µm millipore filter before storage at $4^0$ C. This was done in the laboratory.[64]

*Digestion by Closed System Digester*

7.5 mL of each sample was measured into Teflon decomposition vessels of the digester and to each 2.5 mL of concentrated $HNO_3$ was added. A blank sample consisted of 7.5 mL of de-ionized water to which 2.5 mL of concentrated $HNO_3$ has been added. Digestion was done at a moderately high temperature of 160 $^0$C for 8 hours. The digester was allowed to cool overnight and the digested samples carefully poured out into pre-treated, well- stoppered plastic bottles. The trace metal contents were measured using a Philips PV 9200 flame atomic absorption spectrophotometer.(AAS) Calibration curves were plotted using serially diluted standard solutions of the different metals being determined. These were read in the AAS and the absorption plotted against the concentrations. The characteristics of the machine employed in the measurements of the various metals are shown below:

| *Metal* | *Wavelengths(nm)* | *Detection Limit* | *Sensitivity(ppm)* | *Flame Type* |
|---|---|---|---|---|
| Copper | 324.7 | 0.001 | 0.035 | OA |
| Cobalt | 240.7 | 0.006 | 0.048 | OA |
| Iron | 248.3 | 0.003 | 0.06 | OA |
| Manganese | 279.5 | 0.001 | 0.027 | OA |
| Aluminium | 309.3 | 0.04 | 0.39 | OA |
| Lead | 217.0 | 0.05 | 0.10 | OA |
| Zinc | 213.9 | 0.01 | 0.01 | OA |
| Chromium | 367.9 | 0.01 | 0.05 | OA |
| Nickel | 232.0 | - | 0.59 | OA |

OA = Oxygen - Acetylene. The sensitivities are in mg/L.(ppm)

The detection limit of the AAS for all the trace metals are shown on the Table above.

## 2.3 LABORATORY TREATMENT OF WASTEWATERS

After measurement of the various pollution indicators in the wastewaters, an attempt was made to reduce the levels of the pollutants in selected wastewaters and to explore the possibility of recycling the treated water. Wastewaters from the following industries were used: Pioneer Food Cannery Co. Ltd., Ghana Textiles Manufacturing Co. and Tema Lube Oil Co. Ltd. representing the food, textile and petroleum-based industries respectively.

### 2.3.1 MATERIALS AND PREPARATION OF MATERIALS

#### 2.3.1.1 Soil Samples

Soil samples from Bokazo in Western Region, Ekon, Elmina and Ankaful all in Central Region and Asokwa in the Ashanti Region in Ghana used in the studies, were collected from the Institute of Industrial Research of the Council for Scientific and Industrial Research. Another soil was directly collected from Somanya area in the Eastern Region. This was air-dried and passed through a 600 µm sieve to remove sand and gravel. Deionized water was next added to it and stirred to form a suspension. The suspended soil was decanted off into a plastic bucket and allowed to stand for ten days for the soil to settle. The settled soil was collected, dried, ground with a porcelain mortar and again sieved with a 600 µm plastic sieve.[65]

The former soil samples from the IIR, which had already been treated as above and the Somanya sample were thermally activated by heating in a furnace at a temperature of 1000 $^0$C for one hour. The characteristics of the six inactivated soils were determined at the Soil Research Institute of the CSIR.

### 2.3.1.2 Sea-sand

Sea-sand was collected from a secluded part of the beach at Old Dansoman in Accra and thoroughly washed with tap and deionized water to get rid of the salt. It was acid washed with concentrated hydrochloric acid by soaking overnight to remove carbonates. It was then soaked in deionized water overnight, drained, air-dried and finally oven dried at 110 $^0$C overnight.

### 2.3.1.3 Coconut Husks and Palm Kernel Husks Charcoals

Coconut husks were obtained from the Tema Lorry Station in Accra and chopped into very small pieces. Palm kernel husks were obtained from palm fruits bought at Agbogbloshie Market also in Accra. These were boiled and the fleshy part removed by pounding in a wooden mortar to obtain the nuts. These nuts were dried for a week and cracked open using a stone and the hard husks collected. Both samples were washed well using tap water and sun-dried. The samples were then charred by igniting at 1000 $^0$C for one hour in a furnace. The charred residues of coconut and palm kernel husks were separately boiled in de-ionized water at 110 $^0$C for an hour, to leach out ions formed during the charring. There was further soaking in de-ionized water to dissolve soluble gases like $CO_2$ that might have been trapped in them.[66]

## 2.3.2 TREATMENT OF WASTEWATERS

The raw effluents were analyzed for pollution indicating parameters as already described. The parameters measured were BOD, COD, $PO_4$-P, $NO_3$-N, turbidity, colour, suspended solids and dissolved metals. Measured volumes of the effluents were subjected to various methods of treatment or cleaning as outlined in details below. The treated samples were then analyzed for the same parameters as was done for the raw. One industry was sampled and treated at a time and the treatment completed within one week. This period of time was used because for those factors that changed significantly, the change was very evident after only a few days whilst for those that did not change significantly, there was no need for a further wait.

### 2.3.2.1 Aerobic Treatment

One liter of the wastewater was put into an open plastic bottle, which was kept on a laboratory bench at room temperature and shaken at regular intervals for seven days. The pH, redox potential and temperature were monitored daily. After the seven days, the contents of the bottles were decanted for further analysis.

### 2.3.2.2 Anaerobic Treatment

In the case of anaerobic treatment, the one-liter plastic bottles were filled to the brim with the wastewater and stoppered well to create anaerobic conditions.[6] The pH, redox potential and temperature were measured daily for seven days. On the eighth day, the samples were decanted and the decanted liquid analyzed.

### 2.3.2.3 Sand Filtration

An improvised plastic column was prepared by cutting off the top of a 1.5 liter mineral water bottle. Holes of about 1.5 mm radii were then made in the bottom by using 6-inch nails that had been heated in a charcoal flame. A filter bed of sand about 50 cm in depth was made by packing the treated sea-sand in the plastic mineral water bottle. The top of the plastic bottle was then put at its bottom to direct the filtered water into a receptacle. 100 mL of raw wastewater was passed through a sand filter and the filtrate was collected into another plastic container.

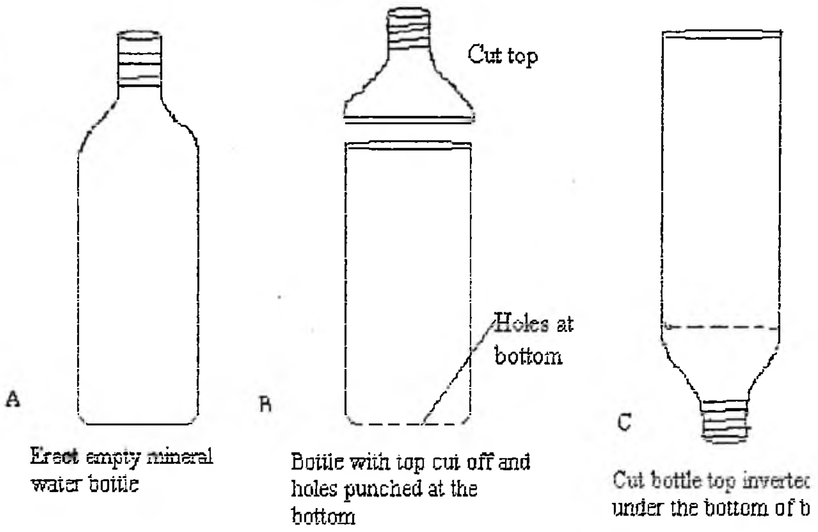

Fig. 1 Preparation of Bottle for Sand Filtration

### 2.3.2.4 Paper Filtration

Watman Qualitative 1 Ca. No. 1001 150 filter paper and a filter funnel were used for the filtration and the filtrate was collected into a well-washed plastic container rejecting the first 100 mL

The filtrate was then analyzed.

### 2.3.2.5 Chemical Coagulation and Sedimentation

The treatments were conducted in a wide mouth polythene bottle into which one liter of the wastewater was poured and one gram of the alum, aluminium ammonium sulphate added. The contents of the bottle were well shaken and left in the open for seven days whilst the pH, redox potential and temperature were measured on a daily basis. After the seventh day, the contents of the bottle were decanted and further analysis for pollutants done immediately.

### 2.3.2.6 Activated Charcoal Treatment

10.0 g of activated charcoal was added to one liter of wastewater in a plastic bottle and the pH, redox potential and temperature monitored daily for seven days after which the contents were decanted and analyzed.

### 2.3.2.7 Palm Kernel Husks and Coconut Husks Charcoals Treatments

10.0 g each of the husks charcoals was added separately to one liter portions of wastewater in plastic bottles and kept for seven days during which period the pH, redox potential and temperature were determined on daily basis after which the contents were decanted and further analyzed.

### 2.3.2.8 Soil Treatment

This treatment was limited to the wastewater of Tema Lube Oil Company because of logistic reasons.

50.0 g of each soil was added to one liter portions of the wastewater in plastic bottles and kept for four days after which the contents of the bottles were decanted and filtered through 45 μm millipore filter membrane. The resulting liquid analyzed for trace metals using AAS after further filtration with 45 μm millipore filter membrane.

# CHAPTER THREE

## RESULTS AND DISCUSSION

### 3.1 RAW EFFLUENTS

The results for the determinations of the levels of the various pollution indicating parameters are presented in Tables 2 to 4. The EPA limits for wastewaters and the WHO limits for drinking water are presented in Table 5.

**TABLE 2 PHYSICAL AND CHEMICAL PARAMETERS - Mean Values for Temperature, pH, Conductivity, DO, BOD, COD, TSS & TDS**

| Sample | Temp. °C | pH | Cond. µS/cm | DO Mg/L | BOD mg/L | COD mg/L | TDS mg/L | TSS mg/L |
|---|---|---|---|---|---|---|---|---|
| TOR$^{A}$ | 28.0 | 7.70 | 54420 | 5.40 | 3.80 | 279 | - | 85.0 |
| TOR$^{B}$ | 31.3 | 7.64 | 54940 | 4.70 | 11.1 | 159 | 56616 | 84.0 |
| TOR$^{C*}$ | 31.2 | 7.42 | 53630 | 3.60 | 12.8 | - | 61595 | 89.0 |
| TOR$^{C}$ | 31.5 | 4.54 | 12610 | 3.40 | 210 | 489 | - | - |
| TOR$^{CT}$ | 31.1 | 6.29 | 47860 | 3.50 | 62.3 | 489 | - | 89.0 |
| SWR | 26.0 | 7.63 | 53100 | 4.60 | 3.60 | 159 | 53789 | 82.0 |
| TCM | 33.3 | 5.61 | 2560 | 0.90 | 4740 | 84461 | 31.9 | 20180 |
| CPC | 32.9 | 5.37 | 290 | 2.67 | 937 | 1806 | 1765 | 420 |
| TLC | 29.5 | 7.00 | 630 | 0.26 | 669 | 1192 | 421 | 292 |
| PFC | 34.2 | 6.60 | 1710 | 0.21 | 375 | 421 | 1492 | 442 |
| BPC | 33.4 | 7.60 | 150 | 2.95 | 76.0 | 1500 | 135 | 3221 |
| GTMC | 37.5 | 10.4 | 5.14 | 2.80 | 80.0 | 637 | 1588 | 60.0 |
| GTP | 47.0 | 13.2 | 3.23 | 3.60 | 547 | 517 | 2497 | 262 |

Cond. - conductivity

Temp. - Temperature

TOR$^{C*}$= Wastewater before shut-down of refinery (used in the discussion)

TOR$^{C}$ = Wastewater after shut-down

TOR$^{CT}$ = Mean values of TOR$^{C*}$ and TOR$^{C}$

TABLE 3 NUTRIENTS AND MAJOR IONS - MEAN VALUES (mg/L)

| Sample | $PO_4$-P | $NO_3$-N | $SO_4$ | $Cl^-$ | K | Na | Ca | Mg |
|---|---|---|---|---|---|---|---|---|
| TOR$^{A}$ | 0.14 | 0.13 | 2258 | 19936 | 480 | 5563 | 4503 | 1396 |
| TOR$^{B}$ | 0.23 | 0.12 | 778 | 20380 | 480 | 5433 | 500 | 1365 |
| TOR$^{C*}$ | 0.27 | - | 525 | 19240 | 515 | 5520 | 401 | 2303 |
| TOR$^{C}$ | 0.18 | - | 905 | 5770 | 0.0 | 3440 | 167 | 681 |
| TOR$^{CT}$ | 0.22 | - | 3150 | 15628 | 423 | 4827 | 211 | 962 |
| SWR | 0.12 | 0.03 | 3150 | 19030 | 530 | 5760 | 399 | 1392 |
| TCM | 8.22 | 0.10 | 74.8 | 26.0 | 195 | 445 | 19.2 | 72.6 |
| CPC | 0.93 | 0.30 | 42.9 | 14.3 | 25.7 | 16.1 | 23.7 | 66.3 |
| TLC | 8.01 | 0.01 | 45.4 | 168 | 30.0 | 108 | 21.1 | 42.1 |
| PFC | 4.21 | 0.13 | 32.0 | 154 | 10.0 | 55.4 | 11.2 | 26.5 |
| BPC | 8.63 | - | 30.0 | 9.5 | - | - | 29.7 | 9.44 |
| GTMC | 8.65 | 0.08 | 31.9 | 110 | 35.0 | 990 | 22.4 | - |
| GTP | 2.87 | 0.001 | 71.4 | 14.3 | 25.0 | 460 | 15.8 | 0.35 |

TABLE 4 MEAN CONCENTRATION OF TRACE METALS (mg/L)

| **Sample** | **Ni** | **Pb** | **Fe** | **Mn** | **Zn** | **Cu** | **Co** | **Cr** | **Al** |
|---|---|---|---|---|---|---|---|---|---|
| TOR$^{A}$ | 0.30 | 0.26 | 0.31 | 0.53 | 0.54 | 0.13 | 0.30 | 0.68 | 0.20 |
| TOR$^{B}$ | 0.26 | 0.25 | 0.58 | 0.46 | 0.50 | 0.14 | 0.30 | 0.68 | 0.64 |
| TOR$^{C*}$ | 0.45 | 0.27 | 0.35 | 0.51 | 0.86 | - | - | - | - |
| TOR$^{C}$ | 0.63 | 0.30 | 6.63 | - | 1.50 | - | - | - | - |
| TOR$^{CT}$ | 0.37 | 0.27 | 3.83 | 0.60 | 0.82 | 0.09 | 0.28 | 0.67 | 0.33 |
| SWR | 0.40 | 0.26 | 0.33 | 0.46 | 0.80 | 0.12 | - | - | - |
| TCM | 0.23 | 0.24 | 3.20 | 0.53 | 1.80 | 0.28 | 0.35 | 0.50 | 2.19 |
| CPC | 0.26 | 0.26 | 1.02 | 0.46 | 0.53 | 0.06 | 0.34 | 0.46 | 0.84 |
| TLC | 0.40 | 0.44 | 2.50 | 0.53 | 1.20 | 1.20 | - | - | - |
| PFC | 0.27 | 0.20 | 0.58 | 0.40 | 1.46 | - | - | - | - |
| BPC | 0.30 | 0.25 | 1.37 | 0.47 | 3.64 | 0.67 | - | - | - |
| GTMC | 0.30 | 0.23 | 1.17 | 0.43 | 0.80 | 1.00 |  |  |  |
| GTP | - | - | 1.50 | 0.25 | 0.70 | 0.73 | - | - | - |

TABLE 5 MEAN AND RANGE VALUES FOR ALL INDUSTRIES COMPARED WITH WHO AND EPA LIMITS

| Parameter | Range | Mean | WHO (1984) | EPA (1997) |
|---|---|---|---|---|
| Temp.(°C) | 28.0 - 47.0 | 34.7 | - | <3 °C above ambient |
| pH | 5.37 - 13.2 | 7.90 | 6.5 - 8.5 | 6.0 - 9.0 |
| Conductivity (µS/cm) | 0.15 - 54940 | 8550 | 700 | 750 |
| Dissolved oxygen | 0.21 - 5.40 | 2.30 | 80% saturation | - |
| Total suspended solids (mg/L) | 60.0 - 20180 | 3120 | - | 50.0 |
| Total dissolved solids (mg/L) | 31.9 - 56616 | 800068 | 1000 | 500.0 |
| Biochemical oxygen demand (mg/L) | 3.8 - 4740 | 929 | < 3.0 | 50.0 |
| Chemical oxygen demand (mg/L) | 159 -84461 | 11317 | | 250 |
| Sulphate (mg/L) | 30.0 - 3150 | 222 | 200 | 10 |

TABLE 5 MEAN AND RANGE VALUES FOR ALL INDUSTRIES COMPARED WITH WHO AND EPA LIMITS (continued)

| **Parameter** | **Range** | **Mean** | **WHO (1984)** | **EPA (1997)** |
|---|---|---|---|---|
| Phosphate (mg/L) | 0.14 – 8.70 | 5.04 | < 0.3 | 2.0 (Total P) |
| Nitrate (mg/L) | 0.00 – 0.13 | 0.10 | 10.0 | 0.1 |
| Calcium (mg/L) | 11.2 - 450 | 77.3 | 200 | |
| Magnesium (mg/L) | 0.35 - 1397 | 229 | 150 | |
| Total hardness (mg/L) | 41.0 - 6882 | 995 | 500 | |
| Chloride (mg/L) | 9.5 - 19936 | 2554 | 250 | 600 initial |
| Nickel (mg/L) | 0.23 – 0.63 | 0.34 | | 0.5 |
| Lead (mg/L) | 0.20 – 0.44 | 0.26 | 0.05 | 0.1 |
| Manganese (mg/L) | 0.40 – 0.64 | 0.47 | 0.1 | |
| Zinc (mg/L) | 0.53 – 3.64 | | 5.0 | 2.0 |
| Cobalt (mg/L) | 0.28 – 0.35 | 0.33 | | |
| Total chromium (mg/L) | 0.46 – 0.68 | 0.54 | | 0.5 |
| Aluminium (mg/L) | 0.20 – 2.19 | | 0.2 | |
| Sodium (mg/L) | 16.1 - 5563 | 1082 | 200 | |
| Potassium (mg/L) | 10.0 - 480 | 113 | 30 | |
| Total iron (mg/L) | 0.31 – 3.20 | 1.72 | 0.3 | 2.0 |
| Copper (mg/L) | 0.06 – 1.2 | 0.41 | 1.0 | 1.0 |

TABLE 6 DIFFERENCES IN THE LEVELS OF POLLUTANTS IN THE WASTEWATER OF TOR AND THE SEAWATER RESERVOIR

| **Parameter** | **TOR$^{A}$** | **Reservoir** | **Difference** |
|---|---|---|---|
| Temperature $^{0}$C | 28.0 | 26.0 | 2.0 |
| pH | 7.70 | 7.63 | 0.07 |
| Conductivity(μS/cm) | 54420 | 53100 | 1320 |
| DO | 5.40 | 4.60 | 0.80 |
| BOD ( mg/L) | 3.8 | 3.60 | 0.20 |
| COD ( mg/L) | 279 | 159 | 120 |
| TSS ( mg/L) | 85.0 | 82.0 | 3.0 |
| $PO_4$ (mg/L) | 0.14 | 0.12 | 0.02 |
| $NO_3$ (mg/L) | 0.13 | 0.03 | 0.10 |
| $SO_4$ (mg/L) | 2258 | 3150 | -892 |
| Cl (mg/L) | 19936 | 19030 | 906 |
| K (mg/L) | 480 | 530 | -50 |
| Na (mg/L) | 5563 | 5760 | 197 |
| Ca (mg/L) | 450 | 399 | 51 |
| Mg (mg/L) | 1397 | 1392 | 5.0 |
| Ni (mg/L) | 0.45 | 0.40 | 0.05 |
| Pb (mg/L) | 0.27 | 0.26 | 0.01 |
| Fe (mg/L) | 0.35 | 0.33 | 0.02 |
| Mn (mg/L) | 0.51 | 0.46 | 0.05 |
| Zn (mg/L) | 0.86 | 0.80 | 0.06 |

## TABLE 6 DIFFERENCES IN THE LEVELS OF POLLUTANTS IN THE WASTEWATER AND SEAWATER RESERVOIR AT TOR

(continued from last page)

| Parameter | $TOR^C$ | Reservoir | Difference |
|---|---|---|---|
| Temperature $^0C$ | 31.2 | 26.0 | 5.2 |
| pH | 7.42 | 7.63 | -0.21 |
| Conductivity | 53630 | 53100 | 530 |
| DO | 3.60 | 4.60 | -1.0 |
| BOD (mg/L) | 12.8 | 3.60 | 9.20 |
| TDS (mg/L) | 61595 | 53789 | 8806 |
| TSS (mg/L) | 89.0 | 82.0 | 7.0 |
| $PO_4$ (mg/L) | 0.27 | 0.12 | 0.15 |
| $SO_4$ (mg/L) | 525 | 3150 | -2625 |
| $Cl^-$ (mg/L) | 19240 | 19030 | 210 |
| K (mg/L) | 515 | 530 | -15.0 |
| Na (mg/L) | 5520 | 5760 | -240 |
| Ca (mg/L) | 401 | 399 | -2.0 |
| Mg (mg/L) | 2303 | 1392 | 1011 |
| Ni (mg/L) | 0.63 | 0.40 | 0.23 |
| Pb (mg/L) | 0.30 | 0.26 | 0.04 |
| Fe (mg/L) | 6.63 | 0.33 | 6.30 |
| Zn (mg/L) | 1.50 | 0.80 | 0.70 |

### 3.1.1 PHYSICAL PARAMETERS - TEMPERATURE, pH, CONDUCTIVITY DISSOLVED OXYGEN AND TOTAL SUSPENDED SOLIDS

The mean temperatures ranged from 28.0 °C in the wastewater from Tema Oil Refinery (TOR) to 47.0 °C in that from Ghana Textiles Printing (GTP) as shown in Table 2 and Fig. 2. In all but two of the industries sampled, the temperatures were around the EPA allowed value of less than 3°C above ambient temperature of 33.0 °C for Tema. The offending industries which had values exceeding the EPA values are Ghana Textiles Printing Co. and Ghana Textiles Manufacturing Co. Ltd., which had average temperatures of 37.5 °C and 47.0 °C respectively. The mean temperature for all the industries was 34.7 °C which is close to the mean ambient temperature. Heated water discharged directly into a water course would significantly increase the temperature of the water. This would affect the aquatic ecosystem by increasing metabolism of the organisms since, biochemical activity often doubles for every 10 °C.[14] This could also reduce the ability of the water to hold dissolved oxygen which is important for the survival of all fauna and flora.[6,17] Generally, solubility of gases in water depends on the temperature of the water. As the temperature increases, the solubility decreases, thus an increase in the temperature of any receiving water would result in the reduction of dissolved oxygen.[6]

Although, an increase in temperature of a few degrees may not be significant, some aquatic ecosystems are very sensitive to minor changes in temperature.[17] The spawning behaviour of many fish is triggered by temperature changes. The discharge of heated water into an estuary can also alter the type of plant food available there. The animal inhabitants of rivers are controlled also by plants that provide them with shelter as well as food. Thus, animals with specific food habits may be eliminated because, the warm water could support different kinds of flora, which can alter or interfere with the food web. Also, at temperatures above 40 $^0$C, some flora and fauna can be killed.[67] Moreover, the temperature can have a direct effect on toxicity of pollutants in that a rise of 10 $^0$C in temperature usually, halves the survival time of a given organism to a particular poison of a specified concentration.[68]

The high temperatures of the wastewaters from the textile industries are due to the scouring process which includes the boiling of the fabric at about 80 $^0$C with a 2 : 1 mixture of sodium hydroxide and sodium trioxocarbonate (IV) to remove starch remains, wax-like materials, fatty substances like pectin and oils.[11] Another source of heat production is the steaming process in which, the fabric is steamed at temperatures up to 200 $^0$C to ensure the fixation of dye.

The pH of an aquatic environment can be changed by added acid or alkali from industrial wastewaters. To maintain a good fish population, it is necessary that the pH of the water is kept in the range 6.7 to 8.6.[69,70] The industries, in order of increasing pH are: Cocoa Processing Co. Ltd., Tuyee Chemical Manufacturing Co., Pioneer Food Cannery, Tema Lube Oil, Tema Oil Refinery, Bridaltrust Paints Co. Ltd., Ghana Textiles Manufacturing Co. and Ghana Textiles Printing Co. as is also shown in Table 2 and Fig. 3. The pH of four of the eight industries, Tema Lube Oil Co., Tema Oil Refinery (exit for API), PFC and Bridaltrust Paints Co. fell within the allowable EPA and the WHO ranges of 6.0 to 9.0 and 6.5 to 8.5 respectively.

The two textile industries sampled, had the highest average pH values of 10.4 and 13.2 respectively which are very basic and well above the EPA upper limit of 9.0. Mintah-Boateng[44] reported a pH of 10.9 for Ghana Textile Printing and 10.7 for Akosombo Textiles Limited (ATL), another textile industry that was not worked on, which shows that the wastewaters from textiles industries are generally basic. This is due to the use of sodium hydroxide during the mercerization process where about 32% sodium hydroxide solution is used to give cloth a glossy and smooth appearance and also in the scouring process as has been outlined in the above paragraph.[11] Tuyee Manufacturing Co. and Pioneer Food Cannery had values below the EPA lower limit value of 6.0. Their wastes are therefore slightly acidic in nature. This may be due to the presence of organic and inorganic acids produced during the oxidation and fermentation of food substances as in maize and tuna fish in Tuyee Manufacturing Co.(TMC) and Pioneer Food Cannery(PFC) wastewaters respectively. Amuzu[71] in 1995 reported a pH of 7.2 for Tema Lube Oil Co. Ltd., which agrees with the 7.0 obtained in this study.

The average for all the pH values in all the wastewaters of all the industries sampled was 7.92 which fell within both the EPA allowed values of between 6.0 - 9.0 for wastewater and WHO allowed values for drinking water of between 6.5 - 8.5.

The pH values of less than 5.0 or greater than 9.0 are known to be harmful to most animal.[6,11,22] Craig[72] in 1975 reported that an aquatic medium with high pH of more than 10 or low pH of less than 2.0 cannot support fish at all. Even within the normal range, the pH has considerable influence on some poisons. For example, whilst $NH_3$ is more poisonous in alkaline than in acid water, cyanide ($CN^-$) is more poisonous in acidic than in alkaline water.[6]

The conductivity values were generally high except for the values for wastewaters from Cocoa Processing Co., TLO and Bridaltrust Paints Co. Ltd. which were below both the EPA value of 750 µS/cm for wastewater and WHO value of 700 µS/cm for drinking water as shown in Table 2 and

Fig. 4. The worst offender was Tema Oil Refinery whose wastewaters had values around 53,000 µS/cm that far exceeded the accepted value of 750 µS/cm. The conductivity of the reservoir of seawater was 53100 µS, which was similar to that of the Refinery itself. It would be suitable if the wastewaters are discharged directly into the sea, but unfortunately, the wastewaters are poured into drains that empty into the Chemu Lagoon resulting in increases in conductivity of the Lagoon waters. The other industries which wastewaters are highly polluting with respect to conductivity are Tuyee, Pioneer Food Cannery, Ghana Textiles Manufacturing Co. and Ghana Textiles Printing.

The wastewaters of Cocoa Processing Co., Tema Lube Oil and Bridaltrust Paints, with conductivities of 290 µS/cm, 630 µS/cm and 150 µS/cm respectively were below the EPA allowed value of 750 µS/cm and thus are to be considered non-polluting. For Tema Lube Oil, Amuzu[71] in 1995 reported a conductivity value of 362 µS/cm. The value of 3280 µS/cm for GTP reported by Mintah-Boateng[44] agreed quite well with that of 3230 µS/cm obtained in this study. When the mean conductivity value for all industries of 8550 µS/cm is compared to the EPA limit of 750 µS/cm, there is cause for alarm because it is more than ten times the EPA limit.

Wastewaters from Pioneer Food Cannery, Tema Lube Oil and Tuyee Manufacturing Co. had very low dissolved oxygen concentrations. The respective values were 0.21, 0.26 and 0.9 mg/L. The mean dissolved oxygen value for all the industries which was 2.30 was appreciable compared to the values for these industries. The dissolved oxygen content for Tema Oil Refinery was generally high, an indication that it contains appreciable quantities of oxygen in spite of the presence of the large amount of organic matter indicated by the quite high value for BOD as shown in Table 2 and

Fig.5. The high values obtained in this study for Tema Oil Refinery, a petroleum-based industry was due to the fast flow of the wastewater at the point of sampling resulting in its aeration. This is supported by the fact that the value was higher than that for the seawater reservoir that was relatively stationary. Very low DO values were obtained for the wastewaters from Tuyee, Tema Lube Oil and Pioneer Food Cannery which also had correspondingly high BOD values, an indication that they contained high concentrations of organic matter. This organic matter in the water sample is broken down through aerobic processes by bacteria and other micro-organisms in the wastewaters using dissolved oxygen in the wastewaters with the production of water and carbon dioxide, hence reducing their oxygen contents greatly.

Compared to Tema Oil Refinery, Tema Lube Oil had a very low DO of 0.26. This could be due to fact that the wastewaters from the latter include some from their kitchen and bathhouses so they must be well inoculated with the right microbes that facilitated the breakdown of the organic matter. In the case of Tuyee, the main raw material used was maize which is not only very rich in starches, but also in the other nutrients like phosphates and nitrates that are needed in the growth of micro-organisms in the wastewaters hence increasing greatly the breakdown of the organic matter. Pioneer Food Cannery, like Tuyee, is also an agro-based industry that produces a lot of easily oxidizable organic matter from using tuna fish as a raw material, so its low DO value is not unexpected, since the breakdown of the organic matter reduces the oxygen content, resulting in a low DO.

Many substances become more toxic as oxygen content of the water falls.[6] Some fishes live only in well-aerated water, hence there is a cause for concern. Whilst the values obtained in this study for GTP and GTMC were 3.6 and 2.8 respectively, those reported by Mintah-Boateng[44] were 4.9

and 0.7 mg/L.

The mean value of suspended solids for all the industries was 3120 mg/L, which far exceeded and is more than 50 times the EPA allowed value of 50.0 mg/L. The most polluting industrial wastewater in this regard is that of an agro-based industry, Tuyee Manufacturing Co., which contains a lot of suspended matter in the order of twenty thousands of milligrams per liter. With a very high BOD, this pointed to a high concentration of organic materials. This means that, when these wastewaters are discharged, they will increase the solid contents of the recipient water bodies which in turn will have an effect on the amount of light that enters the water for aquatic plants to absorb and use for photosynthesis. The amount of plankton for example, could be reduced and this will also reduce the number of fish. Also, the settled solid particles can smother the breeding and feeding sites of fish, which reduces the number of fish and hence affect the food web, as in the case of heated water.[3,5,6,18] The turbidity of the water which is closely related to the concentration of suspended solids also affects the feeding of fishes since most of them hunt by sight.[73] The other effects of inert solids is that they tend to settle out of the water on to the stream beds and so tend to eliminate algae and plants, consequently altering the fauna.[67,74]

## 3.1.2 CHEMICAL PARAMETERS

### BIOCHEMICAL OXYGEN DEMAND (BOD)

The BOD measures the amount of oxygen (mg) that is consumed by a liter of a water sample in a given time, which for $BOD_5$ is 5 days.[14] The reactions involved in this determination are biochemical in nature. Micro-organisms present in the water oxidize organic materials in the water using oxygen that is dissolved in the water (dissolved oxygen), thus reducing the oxygen content of the water. A high BOD value is an indication that the oxygen content of the water is low and vice versa. Apart from Tema Oil Refinery, all the other industries had BOD values that exceeded the EPA allowed value of 50 mg/L as shown in Table 2 and Fig. 6. Wastewaters from all the industries had a mean BOD value of 929 mg/L, which was about twenty times the EPA allowed value. The most polluting ones were the agro-based industries, Tuyee, Cocoa Processing Co. and Pioneer Food Cannery followed by the textiles industries and then the paint industry. For Tema Lube Oil, Amuzu[71] in 1995 reported a BOD value of 11.0 mg/L while the value obtained in this study was 3.80 mg/L. Ghana Textiles Manufacturing Co. and Ghana Textiles Printing with reported values by Mintah-Boateng[44] of 525 and 150 mg/L respectively differ greatly from the values of 80.0 and 547 mg/L obtained in this study. The variations between the results of this study indicate that the nature of industrial effluents varies over time. It may also be an indication of increases or decreases in the efficiency of in-house treatments.

For Tuyee, Tema Lube Oil and Pioneer Food Cannery, the high BOD values obtained correlate with their low dissolved oxygen (DO) contents. For Cocoa Processing Co., in spite of a high DO value, the BOD value was 937 mg/L which was also high. This could be due to the fact that the right microbes for respiration of the organic material were absent or probably, due to the mode of discharge of the wastewater which results in aeration.

## CHEMICAL OXYGEN DEMAND (COD)

Whilst BOD helps in the estimation of the amount of easily oxidizable organic material in a sample of water, chemical oxygen demand (COD) determines the amount of both organic and inorganic materials that are chemically oxidizable. Unlike BOD, COD involves purely chemical oxidation of the oxidizable materials using chemical substances like dichromate and permanganate.[6,14] As far as COD is concerned, almost all the industries had high values. The only exception was again Tema Oil Refinery with a COD of 279 mg/L, which was quite close to the EPA limit of 250 mg/L. The most polluting industry with respect to COD was Tuyee with a value of 84461 mg/L as presented in Table 2 and Fig. 7. This value far exceeded the 250 mg/L upper limit acceptable to EPA. Next in polluting potential was Bridaltrust Company with a high COD value of 1500 mg/L, with Tema Lube Oil, Cocoa Processing Co., also producing considerable amount of COD pollution. The high COD value in spite of the comparably low BOD value suggested that the wastewater contained a lot of inorganic oxidizable materials. For Tema Lube Oil, Amuzu[71] reported a COD of 96.0 mg/L in 1995 but the value obtained here was 1192 mg/L. The wastewaters from Tema Oil Refinery had the least mean COD, which was far below the acceptable limit. The mean value for all the industries of 11317 mg/L was more than twenty times the EPA allowed value, which is quite threatening.

### 3.1.3 TOTAL DISSOLVED SOLIDS (TDS) AND TOTAL SUSPENDED SOLIDS (TSS)

In this instance, the extent of total dissolved solids pollution in increasing order was, Tema Oil Refinery, Ghana Textiles Printing Co., Cocoa Processing Co., Ghana Textiles Manufacturing Co., Pioneer Food Cannery, Tema Lube Oil Co., Bridaltrust Paints Co. and Tuyee Manufacturing Co. Here, all the industries are potential pollution sources of suspended solids as seen in Table 2 and Fig. 9. Compared with the EPA limit of 50.0 mg/L, the industry that had the lowest value was Ghana Textiles Manufacturing Co. with a level of 60 mg/L, a difference of 10 units on the higher side from the EPA value. The TDS and the TSS values of 422 mg/L and 292 mg/L of this study when compared to 252 and 62.0 mg/L obtained by Amuzu[71] in 1995 for Tema Lube Oil Co., showed a high increase which is quite alarming. However, as has been already pointed out, this could be a result of the breakdown of their American Petroleum Institute (API) plant. The value of GTP of 262 mg/L for TSS is rather high compared with what was obtained by Mintah-Boateng[44] which was 60.0 mg/L.

The EPA allowed value for total dissolved solids (TDS) is 500 mg/L. Judging from the values in Table 2 and Fig. 8, the offending industries are therefore in order of decreasing gravity of polluting potential, Tema Oil Refinery, Ghana Textiles Printing, Cocoa Processing Co., Ghana Textiles Manufacturing Co., and Pioneer Food Cannery. The effluents of Tuyee, Tema Lube Oil and Bridaltrust Paints wastewaters had dissolved solid levels that fell below the EPA limit as shown in Table 2 and Fig. 8. The solids in Tema Oil Refinery may be mostly sodium and potassium salts as shown by the large values of potassium and sodium concentrations. They could also contain some magnesium and calcium salts, because the levels of these parameters were also quite high. The TDS values for both Ghana Textiles Manufacturing Co. and Ghana Textiles Printing are significantly high due to the large amount of dye stuffs that they contain which particles were able to pass through the 45 μm filter used in the determination of the parameter. The quite high value recorded for Pioneer Food Cannery Co. is from blood and other nutrient materials in the main raw material that is tuna fish that were dissolved in the wastewater. Tuyee had the lowest level of dissolved solids which could be nutrients like nitrates, phosphates, peptides, amino acids etc. present in maize, the main ingredient.

The mean value of suspended solids for all the industries was 3120 mg/L which, far exceeded and is more than 50 times the EPA allowed value of 50.0 mg/L. The most polluting industrial wastewater in this regard is that of an agro-based industry, Tuyee Manufacturing Co., which contains a lot of suspended matter in the order of twenty thousands of milligrams per liter. With a very high BOD, this pointed to a high concentration of organic materials. This means that, when these wastewaters are discharged, they will increase the solid contents of the recipient water bodies which in turn will have an effect on the amount of light that penetrates the water thus making it difficult for aquatic animals to obtain enough light for photosynthesis.

### 3.1.4 NUTRIENTS - NITRATE AND ORTHOPHOSPHATE

In Table 3 and Figs. 10, 11 & 12 are presented the levels of the above mentioned parameters. The levels of orthophosphate ranged from 0.14 mg/L in the effluent of TOR to 8.65 mg/L in that of GTMC. With the exception of TOR, all the other industries had concentrations of orthophosphate that exceeded the WHO limit of <0.3 mg/L. The EPA limit for total phosphorus is 2.0 mg/L. This is made up of the three forms in which phosphorus can exist in effluents that is organically bonded phosphorus, polyphosphates and orthophosphates.[13] For most of the industries, the concentration of orthophosphate alone exceeded the EPA limit for total phosphate. This is an indication that all the industries with the exception of Tema Oil Refinery were highly polluting in orthophosphate. On the contrary, the phosphate concentration in the wastewater from Tema Lube Oil, another petroleum-based industry was one of the highest, which could be due to the additives used to blend the base oil. The values for Tuyee and Pioneer Food Cannery are not unexpected, since both of them are agro-based industries and maize and fish, the main raw materials for the industries are rich in phosphates. It has been mentioned elsewhere in this text that, the wastewaters from their kitchen and bath-houses also discharge into the same drains. These can contain detergents, which are very rich in organic polyphosphates, which upon hydrolysis increase the inorganic phosphate content of the wastewaters.

Nitrate concentrations were moderate and the mean value of 0.10 mg/L was exactly equal to that allowed by EPA. This is an indication that the concentrations in the wastewaters of the industries collectively were not threatening as far as this parameter is concerned. The individual values for some of the industries were below the EPA limit of 0.1 mg/L, but the wastewaters from Tema Oil Refinery, Cocoa Processing Co. and Pioneer Food Cannery were higher. Also, the concentrations for Tuyee and Ghana Textiles Printing, though a little lower than the EPA limit, were close enough to merit attention. The above parameters, orthophosphate and nitrate are nutrients with high levels in wastewaters can result in greater biological productivity and may eventually upset the ecosystem of the receiving waters.[13]

## 3.1.5 MAJOR IONS

### CHLORIDE

The EPA limit for chloride in wastewaters is of 600 mg/L but for WHO, the limit for drinking water is 250 mg/L. According to the results in Table 3 and Fig. 13, the chloride concentrations in all the industrial wastewaters with the exception of TOR were below the EPA and WHO allowed values. The values ranged from 9.5 mg/L in the effluent from Bridaltrust Paints to 19936 mg/L in that of Tema Oil Refinery with a mean of 2554 mg/L.

### POTASSIUM

As shown in Table 3 and Fig. 14 & 15, potassium concentrations in wastewaters from Ghana Textiles Printing, Pioneer Food Cannery, Cocoa Processing Co. and Tema Lube Oil were below or were equal to the WHO limit of 30 mg/L. Unfortunately, the EPA does not have any limit for potassium presently, so the WHO limit for drinking water was used for the discussion. The concentration of potassium for Ghana Textiles Manufacturing Co. of 35.0 mg/L, was also close to the WHO limit. The value for Tuyee was very high, about seven times the allowed value. Also, for Tema Oil Refinery, the concentration was about sixteen times higher but lower than the value for the unused sea-water. The mean concentration for all the industries of 113 mg/L far exceeded the WHO limit which makes industries a potential source of potassium pollution. Potassium is incorporated into cell material, so it can encourage the growth of micro-organisms.

## SODIUM

The EPA does not have any limits for the concentration of sodium. The mean concentration for all the industries of 1082 mg/L is about five times the WHO allowed value of 200 mg/L for drinking water. Individually too, except for Pioneer Food Cannery, Tema Lube Oil and Cocoa Processing Company, all the others exceeded the WHO limit. The Tema Oil Refinery value far exceeded the allowed value which was not surprising because the wastewater is obtained from the sea-water used for the cooling process. The sea-water already contains high concentrations of sodium and potassium salts in addition to calcium and magnesium salts. The values for the two textiles industries, Ghana Textiles Manufacturing Co. and Ghana Textiles Printing were also higher than the WHO limit but much lower than the value for Tema Oil Refinery. The presence of moderately high sodium content in the wastewaters from Ghana Textiles Manufacturing Co. and Ghana Textiles Printing is due to the use of large amounts of sodium salts like chlorate and hypochlorite as oxidants and hydroxide in mercerization.[11] A similarly quite high value for Tuyee can be attributed to the use of sodium hydroxide in the steeping of the milled maize to extract the starch that is used in the production of industrial starch.[75]

**CALCIUM**

The mean concentrations of calcium for all industries of 77.3 mg/L was far below the WHO limit of 200 mg/L. Individually however, the concentration for Tema Oil Refinery was the only one that exceeded this value as presented in Table 3 and Figs. 16, 17 & 18.

**MAGNESIUM**

Also, as far as magnesium is concerned, Tema Oil Refinery was the only industry that exceeded the WHO limit of 150 mg/L. With a mean value for magnesium of 229 mg/L, the WHO limit has been exceeded. As already indicated above, wastes from TOR are disharged through the seawater used for cooling.

**SULPHATE**

With a mean of 222 mg/L, the sulphate levels ranged from 30.0 to 3150 mg/L. None of these values were below the EPA allowed value of 10.0 mg/L. Again, the Tema Oil Refinery levels were the highest, in the magnitude of thousands of milligrams per litre. This was expected, because sea-water is used for the cooling during the refining of petroleum and this already contains a lot of sulphates.

### 3.1.6 TRACE METALS

Compared to the EPA and WHO limits, the levels of the metals were found to be generally high and hence, the industrial wastewaters are quite polluting in trace metals as indicated in Table 4 and Fig. 19 - 27.

#### 3.1.6.1 Nickel (Ni)

With a EPA allowed value of 0.5 mg/L, the mean concentration of Ni in the industrial wastewaters was 0.30 mg/L. The individual levels ranged from 0.23 - 0.37 mg/L. The values did not exceed the allowed value but were high enough for the industries to be potential sources of this trace metal pollution. The least polluting industry was Tuyee, an agro-based industry. Generally, the most polluting group of industries was the petroleum-based, followed by the agro-based and the chemical and textiles industries. In a study in Nigeria in 1991, Osibanjo[76] reported a level of < 0.010 mg/L in the wastewaters of textiles industries in Nigeria. Thus, the value of 0.30 mg/L obtained for Ghana Textiles Manufacturing Co. was higher but still below the EPA limit.

### 3.1.6.2 Lead (Pb)

Lead is highly poisonous to man and other living organisms. However, it has been reported by Van Loon[5] to be probably essential in low quantities. The concentrations of Pb were generally high with a mean value of 0.26 mg/L for all the industries. The values for the various industries ranged from 0.20 mg/L to 0.44 mg/L as compared to the WHO and EPA limits of 0.05 and 0.1 mg/L respectively. All the industries are therefore potential sources of Pb pollution, the most polluting and the least polluting being Tema Lube Oil, a petroleum based industry and Pioneer Food Cannery, an agro-based industry respectively. Just as for nickel, the most polluting industrial group is the petroleum-based industries, then the chemical and textiles and finally the agro-based industries. Biney[59] and Osibanjo[76] reported lead concentrations of 0.65 mg/L and < 0.10 mg/L in the wastewaters of textiles industries in Ghana and Nigeria respectively. Osibanjo[76] also reported 0.20 mg/l for the oil industry whilst the values quoted for Tema Oil Refinery and Tema Lube Oil were 0.27 and 0.44 mg/L respectively. That of Tema Oil Refinery was in agreement unlike the concentration for Tema Lube Oil.

### 3.1.6.3 Iron (Fe)

With a mean value of 1.72 mg/L and a range of 0.31 to 3.83 mg/L, the values of Fe for all the industries exceeded the WHO allowed value of 0.3 mg/L. The most polluting wastewater was TOR$^C$ which was the wastewater from the API of Tema Oil Refinery with a level of 3.83 mg/L, followed by Tuyee with a value of 3.20 mg/L and then Tema Lube Oil with a level of 2.5 mg/L. Tema Oil Refinery and Tema Lube Oil are petroleum-based and therefore, it can be concluded that the petroleum-based industries are the most potentially polluting of all the industries sampled. The least polluting industry was Pioneer Food Cannery, an agro-based industry with a level of 0.58 mg/L although CPC and TMC, the other agro-based industries had quite high values. Biney[59] and Osibanjo[76] reported 0.31 mg/L and 0.50 mg/L in textiles effluents in Ghana and Nigeria respectively. Osibanjo[76] also reported 1.45 mg/L for the oil refinery. The allowed value for Fe by EPA is 2.0 mg/L. The industries that exceeded this value were TOR, Tuyee and Tema Lube Oil.

### 3.1.6.4 Manganese (Mn)

The concentration of manganese in all the wastewaters exceeded the WHO maximum limit of 0.1 mg/L. The range was 0.25 to 0.60 mg/L and the mean of 0.46 mg/L was about five times the allowed value. The most polluting wastewater was TOR$^C$ from the API of Tema Oil Refinery with a value of 0.60 mg/L, followed by TOR$^A$ of Tema Lube Oil with a value of 0.53 mg/L. Tema Oil Refinery and Tema Lube oil are petroleum based so it can be deduced that the petroleum based industries are the most polluting in Mn. The least polluting industry was Pioneer Food Cannery and Cocoa Processing Co., which are agro-based. TMC, another agro-based industry had values that were comparable to those of the petroleum-based industries. This may be due to contamination from the wearing away of the metal from the grinding mills used for grinding the corn which the caustic soda solution used for the extraction of the starch could have dissolved. Whilst the levels for the textiles industries were 0.43 and 0.25 mg/L for GTMC and GTP respectively, Osibanjo[76] reported 0.83 mg/L for the textiles industries in Nigeria.

### 3.1.6.5 Zinc (Zn)

The various values ranged from 0.70 to 3.64 mg/L with a mean of 1.28 mg/L. The EPA limit for zinc of 2.0 mg/L was exceeded by only the wastewater from Bridaltrust Paints Co. Ltd. with a concentration of 3.64 mg/L. Concentrations in the various industrial wastewaters, however fell below the WHO limit of 5.0 mg/L.

The paint industry had the highest zinc concentration followed by Pioneer Food Cannery, an agro-based industry. In spite of the fact that they all fell below the EPA limit for the wastewater from Bridaltrust Paints, some of the industries had levels that demand attention. These were Tuyee, Pioneer Food Cannery and Tema Lube Oil Co. with values of 1.80, 1.46 and 1.20 respectively mg/L. Biney[59] and Osibanjo[76] reported values of 0.50 mg/L and 0.05 mg/L for the textiles industries in Ghana and Nigeria respectively whilst for the petroleum (oil) industry, Osibanjo[76] reported 0.25 mg/L. The values of 0.80 and 0.70 mg/L reported for GTMC and GTP are quite comparable to that of Biney.[59]

### 3.1.6.6 Copper (Cu)

The values ranged from 0.06 to 1.2 mg/L, with a mean level of 0.41 mg/L. Individually, the WHO and EPA limits of 1.0 mg/L was equalled only by the wastewater from GTMC. The lowest concentrations of Cu were obtained in the wastewaters from Tema Oil Refinery and Cocoa Processing Co.

Biney[59] and Osibanjo[76] reported values of 2.75 mg/L and 0.12 mg/L for the textiles industries in Ghana and Nigeria respectively. The values obtained in this study were not however in agreement with these values for the petroleum-based industries, the values were in agreement with the value of 0.14 mg/L reported by Osibanjo.[76]

### 3.1.6.7 Cobalt (Co)

The values ranged from 0.28 to 0.35 mg/L and the mean was 0.33 mg/L. The industries that had the highest concentrations of cobalt were Tuyee and Cocoa Processing Co. with values of 0.35 and 0.34 mg/L respectively. The least values in this case were recorded for Tema Oil Refinery, a petroleum industry. Unfortunately, the levels for the other industries could not be determined because the AAS developed problems. Osibanjo[76] reported less than 0.10 mg/L for the textiles industries in Nigeria, and this could be an indication of generally low levels of Co in industrial wastewater. No literature values were obtained for Ghana. The WHO and EPA values too were not available for comparison.

### 3.1.6.8 Chromium (Cr)

The range was 0.46 to 0.68 mg/L with a mean of 0.54 mg/L. The WHO and EPA limits of 0.5 mg/L for total chromium was exceeded by Tema Oil Refinery and Tuyee which are petroleum and agro-based industries respectively. Cocoa Processing Co., an agro-based industry had a value of 0.46 mg/L which was just slightly lower than the WHO and EPA limits. The mean value of 0.54

mg/L for all the industries was just a little higher than the allowed value of 0.5 mg/L for both EPA and WHO. Chromium ions ($Cr^{+6}$) are common contaminant of drinking water while $Cr^{+3}$ is not so common.

### 3.1.6.9 Aluminium (Al)

Individually, all the values exceeded the WHO allowed value of 0.2 mg/L. The industry with the highest level of Al was Tuyee. This is not very surprising; strong caustic soda solution used to extract starch from the milled corn may dissolve aluminium, an amphoteric metal that may be present in the metallic parts of the corn mills as well as the vats used for steeping of maize. The levels of Al for the individual industries ranged from 0.01 to 2.19 mg/L. The mean of 1.15 mg/L was about six times the WHO value.

## 3.2 LABORATORY TREATED WASTEWATERS

Table 7 shows the % decomposition of the soils and Table 8, the texture, phosphorus and potassium contents of the soils. The levels of pollutants in the untreated and treated wastewaters are shown in Tables 9 to 16 while EPA and WHO allowed limits for waste waters and drinking water respectively are shown in Table 5. Variations in turbidity (which has a direct relationship with suspended solids), BOD, $PO_4$-P and $NO_3$-N for the different types of treatments for each industry are shown in Fig. 28 to 39 for comparison. The values quoted for the treated wastewaters are for the last day.

**TABLE 7 THERMAL ACTIVATION OF SOILS - WEIGHINGS**

| Source of soil | Wt. Of soil (g) | Wt. Of residue (g) | Wt. Of decomposed portion (g) | % decomposition |
|---|---|---|---|---|
| Ankaful | 50.0006 | 43.4630 | 6.54 | 13.1 |
| Bokazo | 50.0000 | 47.0527 | 2.95 | 5.90 |
| Elmina | 50.0003 | 43.5564 | 6.44 | 12.9 |
| Somanya | 50.0002 | 44.6990 | 5.30 | 10.6 |
| Ekon | 50.0006 | 42.9358 | 7.06 | 14.1 |
| Asokwa | 50.0329 | 44.7207 | 5.31 | 10.6 |

**TABLE 8 PHYSICAL CHARACTERISTICS, POTASSIUM AND PHOSPHORUS CONTENTS OF THE SOILS**

| Soil Location | % Sand | % Silt | % Clay | Texture | P | K |
|---|---|---|---|---|---|---|
| Somanya | 5.81 | 6.97 | 87.0 | Clay | 2.90 | 19.4 |
| Bokazo | 14.9 | 67.0 | 18.2 | Silt/Loam | 10.9 | 4.61 |
| Asokwa | 8.10 | 9.29 | 82.6 | Clay | 1.34 | 9.44 |
| Ankaful | 9.53 | 58.2 | 32.3 | Silt/Clay/Loam | 2.08 | 12.7 |
| Ekon | 11.1 | 15.6 | 73.2 | Clay | 8.62 | 85.0 |
| Elmina | 10.9 | 8.64 | 80.4 | Clay | 1.49 | 1156 |

The units of potassium and phosphorus are mg/g

TABLE 9 SOME PHYSICAL, CHEMICAL PARAMETERS AND NUTRIENT LEVELS BEFORE AND AFTER TREATMENTS - TEMA LUBE OIL CO. LTD

| Treatment | pH | Cond. µS/cm | Turb. (NTU) | Colour (TCU) | BOD (mg/L) | $PO_4$-P (mg/L) | $NO_3$-N mg/L |
|---|---|---|---|---|---|---|---|
| None | 6.72 | 411 | 108 | 250 | 220 | 8.72 | 0.0055 |
| Aerobic | 7.24 | 411 | 8.30 | 25.0 | 21.0 | 7.83 | 0.0022 |
| Anaerobic | 6.56 | 424 | 34.1 | 45.0 | 20.0 | 6.80 | 0.0029 |
| Sand filtration | 7.82 | 164 | 2.40 | 5.00 | 13.0 | 0.37 | 0.0014 |
| Paper filtration | 7.62 | 335 | 22.8 | 75.0 | 16.0 | 1.55 | 0.0045 |
| Alum | 4.94 | 702 | 2.90 | 10.0 | 10.5 | 0.11 | 0.0031 |
| Act. charcoal | 7.26 | 592 | 7.40 | 20.0 | 12.0 | 3.50 | 0.0036 |
| PKC | 7.28 | 336 | 27.0 | 75.0 | 13.0 | 3.07 | 0.0028 |

NTU = Nephelometric Turbidity Units

PKC = Palm kernel husks charcoal

Cond. = conductivity

Turb. = Turbidity

TABLE 10 SOME PHYSICAL, CHEMICAL PARAMETERS AND NUTRIENT LEVELS BEFORE AND AFTER TREATMENTS - PIONEER FOOD CANNERY CO.

| **Treatment** | **pH** | **Cond. µS/cm** | **Turbid (NTU)** | **Colour (TCU)** | **BOD mg/L** | **$PO_4$ -P mg/L** | **$NO_3$-N mg/L** |
|---|---|---|---|---|---|---|---|
| None | 6.52 | 1465 | 75.0 | 500 | 170 | 21.2 | 0.61 |
| Aerobic | 8.02 | 1055 | 31.0 | 125 | 105 | 16.7 | 0.61 |
| Anaerobic | 6.41 | 1380 | 34.0 | 100 | 110 | 16.5 | 0.59 |
| Sand filtration | 6.89 | 66.8 | 4.50 | 2.50 | 7.75 | 0.65 | 0.59 |
| Paper filtration | 6.72 | 1320 | 72.0 | 485 | 160 | 22.0 | 0.60 |
| Alum | 5.34 | 1204 | 73.0 | - | 135 | 12.1 | 0.58 |
| Act. charcoal | 7.52 | 998 | 33.0 | - | 16.5 | 12.3 | 0.60 |
| PKC | 7.59 | 562 | 47.0 | - | 18.0 | 11.9 | 0.59 |

PKC = Palm kernel husks charcoal

## TABLE 11 SOME PHYSICAL,CHEMICAL PARAMETERS AND NUTRIENT LEVELS BEFORE AND AFTER TREATMENTS - GHANA TEXTILES MANUFACTURING CO.

| Treatment | pH | Cond. µS/cm | Turb. (NTU) | Colour (TCU) | BOD (mg/L) | $PO_4$-P (mg/L) | $NO_3$-N (mg/L) |
|---|---|---|---|---|---|---|---|
| None | 11.7 | 1722 | 48.6 | 6000 | 190 | 4.06 | 0.71 |
| Aerobic | 9.60 | 1175 | 29.0 | 6000 | 150 | 3.72 | 0.81 |
| Anaerobic | 11.6 | 1150 | 44.0 | 6000 | 110 | 3.66 | 0.76 |
| Sand filtration | 8.10 | 153 | 1.30 | 40.0 | 2.00 | 0.46 | 1.00 |
| Paper filtration | 11.4 | 1695 | 46.5 | 6000 | 175 | 0.40 | 0.70 |
| Alum | 8.68 | 1403 | 18.0 | 3580 | 25.0 | 0.88 | 0.62 |
| Act. charcoal | 9.62 | 1274 | 17.4 | - | 25.0 | 3.42 | 0.69 |
| PKC | 9.80 | 1098 | 23.4 | - | 145 | 3.39 | 0.63 |
| Ekon clay | 10.1 | 1287 | 9.70 | - | - | 3.30 | 0.74 |
| Elmina clay | 9.72 | 1186 | 19.5 | - | - | 3.22 | 0.86 |

## TABLE 12 MEAN CONCENTRATIONS OF TRACE METALS BEFORE AND AFTER TREATMENTS - TEMA LUBE OIL CO. (mg/L)

| Treatment | Fe | Pb | Ni | Co | Cu | Zn |
|---|---|---|---|---|---|---|
| None | 0.19 | 0.03 | 0.07 | bdl | 0.011 | 0.17 |
| Aerobic | bdl | bdl | 0.065 | bdl | 0.011 | 0.09 |
| Anaerobic | bdl | bdl | bdl | bdl | 0.001 | 0.11 |
| Sand filtration | bdl | 0.11 | bdl | bdl | 0.004 | 0.11 |
| Paper filtration | bdl | bdl | 0.026 | bdl | 0.001 | 0.08 |
| Alum | 1.31 | bdl | 0.13 | bdl | 0.001 | 0.18 |
| Act. charcoal | bdl | bdl | 0.062 | bdl | bdl | 0.08 |
| PKC | bdl | bdl | bdl | bdl | bdl | 0.09 |

bdl = below detection level

TABLE 13 AVERAGE LEVELS OF TRACE METALS BEFORE AND AFTER TREATMENT WITH SOILS (mg/L) - TEMA LUBE OIL CO.

| Soil | Fe | Pb | Ni | Cu | Zn |
|---|---|---|---|---|---|
| None(Raw wastewater) | 0.19 | 0.03 | 0.07 | 0.011 | 0.17 |
| Ankaful | bdl | bdl | bdl | bdl | 0.19 |
| Asokwa | bdl | bdl | bdl | bdl | 0.15 |
| Bokazo | bdl | bdl | bdl | bdl | 0.23 |
| Ekon | bdl | bdl | bdl | bdl | 0.19 |
| Elmina | bdl | bdl | bdl | bdl | 0.18 |
| Somanya | bdl | bdl | bdl | bdl | 0.35 |

TABLE 14 PERCENTAGE CHANGES IN VALUES OF WASTEWATER PARAMETERS AFTER TREATMENTS - TEMA LUBE OIL

| Treatment | pH | Conductivity | Turbidity | Colour | $BOD_5$ | $PO_4$-P | $NO_3$-N |
|---|---|---|---|---|---|---|---|
| Aerobic | 7.74 | 0 | 92.3 | 90 | 90.5 | 10.2 | 60.0 |
| Anaerobic | 2.38 | 3.18 | 68.5 | 82 | 90.9 | 22.0 | 47.3 |
| Sand filtration | 16.4 | 60.1 | 97.8 | 98 | 94.1 | 95.8 | 74.6 |
| Paper filtration | 13.4 | 18.5 | 78.9 | 70 | 92.7 | 82.3 | 18.2 |
| Alum | 26.5 | 70.8* | 97.3 | 96 | 95.2 | 98.7 | 43.6 |
| Activated charcoal | 8.04 | 44.0 | 93.2 | 92 | 94.6 | 59.9 | 34.6 |
| Palm kernel husks | 8.33 | 18.3 | 75.1 | 70 | 94.1 | 64.9 | 49.1 |

- = increase

TABLE 15 PERCENTAGE CHANGES OF WASTEWATER PARAMETERS AFTER TREATMENTS - PIONEER FOOD CANNERY CO. LTD.

| Treatment | pH | Conductivity | Turbidity | Colour | $BOD_5$ | $PO_4$-P | $NO_3$-N |
|---|---|---|---|---|---|---|---|
| Aerobic | 23.0* | 28.0 | 58.7 | 75.0 | 38.2 | 21.5 | - |
| Anaerobic | 1.69 | 5.80* | 54.7 | 80.0 | 35.3 | 22.3 | 4.08 |
| Sand filtration | 5.64 | 95.4 | 69.8 | 99.5 | 95.4 | 97.0 | 3.92 |
| Paper filtration | 3.07 | 9.9 | 3.00 | 2.90 | 5.88 | 7.31 | 2.45 |
| Alum | 18.1* | 17.8 | 75.4 | - | 92.1 | 43.0 | 4.89 |
| Act. charcoal | 15.3* | 31.9 | 56.0 | - | 90.3 | 42.1 | 2.77 |
| PKC | 16.4* | 61.6 | 37.3 | - | 89.4 | 43.8 | 3.59 |

PKC = Palm kernel husks charcoal * = increase

TABLE 16 PERCENTAGE CHANGE IN VALUES OF WASTEWATER PARAMETERS AFTER TREATMENTS - GHANA TEXTILES MANUFACTURING CO.

| Treatment | pH | Conductivity | Turbidity | Colour | $BOD_5$ | $PO_4$-P | $NO_3$-N |
|---|---|---|---|---|---|---|---|
| Aerobic | 17.8 | 31.8 | 40.3 | 0 | 21.1 | 8.37 | 18.7 |
| Anaerobic | 0.51 | 33.2 | 9.47 | 0 | 42.1 | 8.73 | 23.3 |
| Sand filtration | 30.7 | 91.1 | 97.3 | 99.3 | 99.0 | 88.6 | 10.9 |
| Paper filtration | 2.48 | 1.57 | 4.32 | 0 | 7.89 | 10.0 | - |
| Alum | 25.7 | 18.4 | 63.0 | 40.3 | 86.8 | 78.3 | 37.3 |
| Activated charcoal | 17.6 | 74.0 | 64.2 | - | 86.8 | 15.8 | 29.7 |

The discussions will be mainly on the effect the various treatment methods had on BOD, nitrogen and phosphorus salts, suspended solids and trace metals in this work since present day treatment of effluents focuses on the reduction of these parameters.[13] Results are shown in Tables 7 to 16 and Figs. 28 - 39.

### 3.2.1 AEROBIC TREATMENT

When the three wastewaters were aerated, the BOD values for Tema Lube Oil was reduced from 220 mg/L to 21.0 mg/L, a decrease of 90.5 %. For Pioneer Food Cannery Co., the decrease was from 170 mg/L to 105 mg/L, which amounted to a percentage decrease of 38.2. In the case of Ghana Textiles Manufacturing Co., the decrease was 21.1 % from 190 mg/L to 150 mg/L. These results show that BOD reduction by aeration for the three industries was highest for the wastewater from Tema Lube Oil. The Tema Lube Oil wastewater sampled contained domestic wastewater from their kitchen as well as their bathrooms, so it is more likely to be dosed with more of the micro-organisms that are necessary for the breakdown of the organic materials in the wastewaters.

A close look at Tables 9 - 16 shows that there is generally a direct relationship between the turbidity and BOD values, the BOD increases as turbidity increases and vice versa.

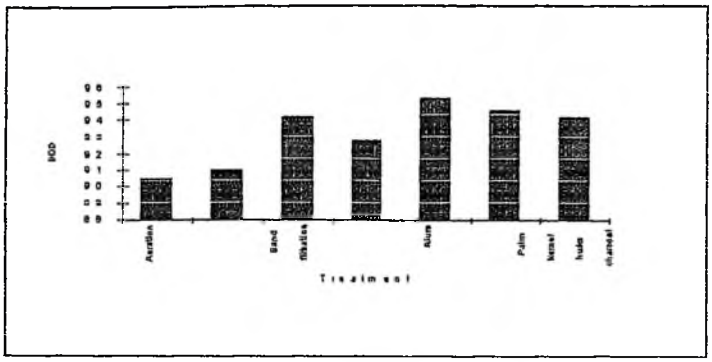

Fig. 28 - % Change of BOD with Treatment for TLC

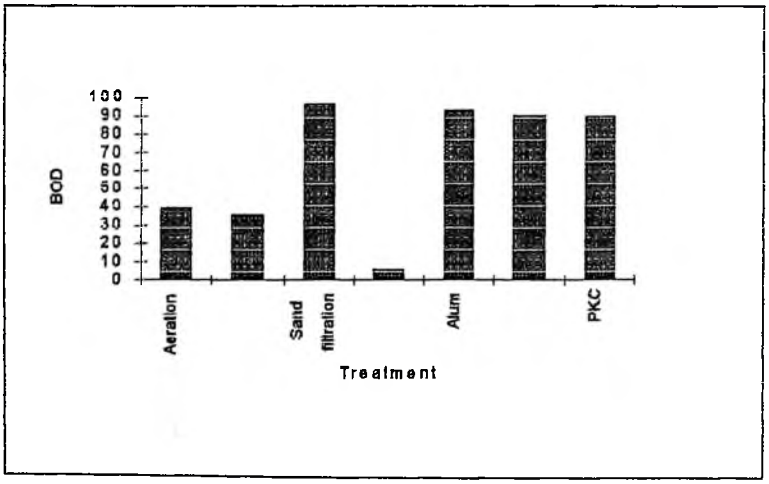

Fig. 29 - % Change of BOD with Treatment for PFC

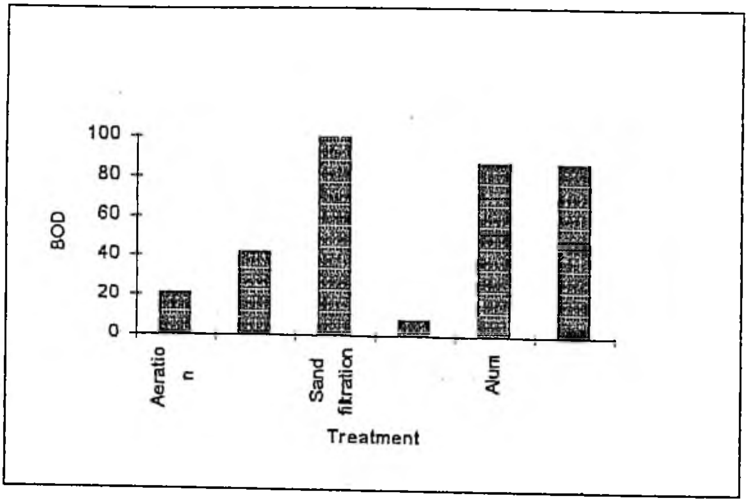

Fig. 30 - % Change of BOD with Treatment for GTMC

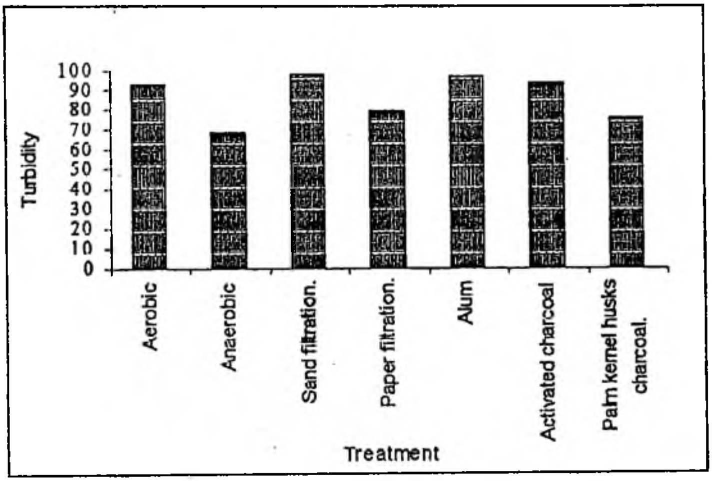

Fig. 31 - % Change of Turbidity with treatment for TLO

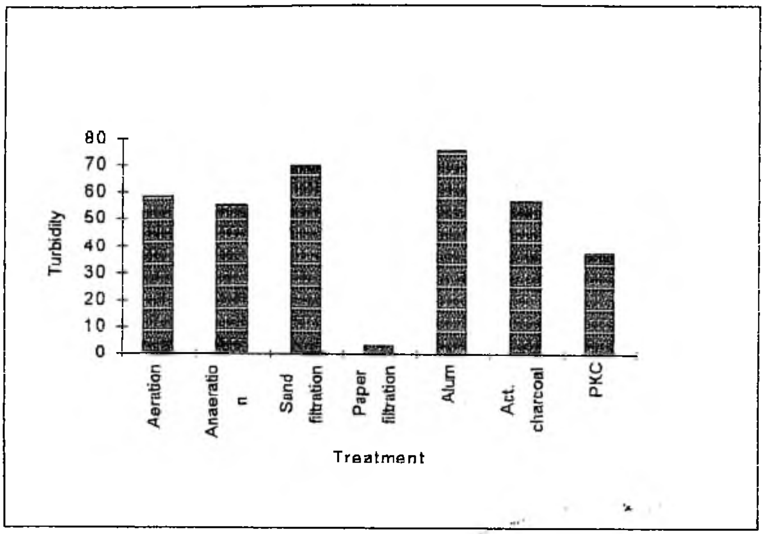

Fig. 32 - % Change of Turbidity with treatment for PFC

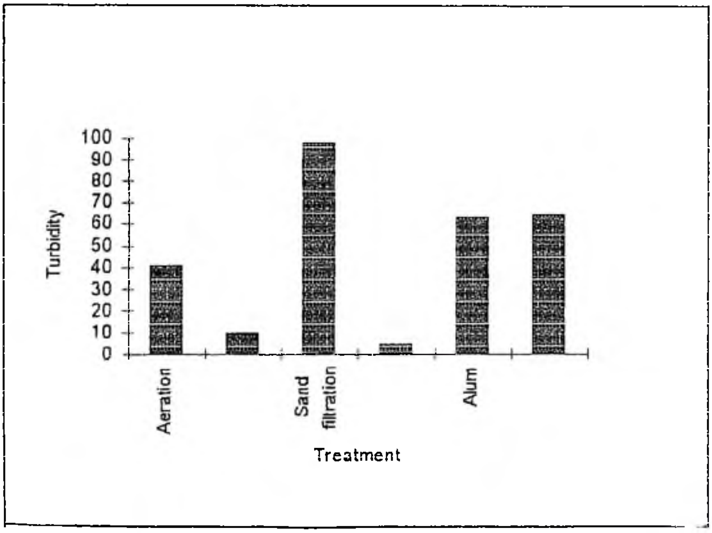

Fig. 33 - % Change of Turbidity with Treatment for GTMC

The turbidity is also closely related to the suspended solids; the higher the suspended solids, the higher the turbidity of a wastewater. From this, it can be deduced that, the amount of suspended solids is highest in Tema Lube Oil since it had the highest turbidity, followed by Pioneer Food Cannery and finally by Ghana Textiles Manufacturing Co. As expected, the BOD of Tema Lube Oil was highest but that for GTMC was higher than for Pioneer Food Cannery.

When aerobically treated, the turbidity of the wastewater from Tema Lube Oil decreased from 108 to 8.30, a decrease of 92.3 %, that of Pioneer Food Cannery decreased from 75.0 NTU to 31.0 NTU, a percentage of 58.7. For Ghana Textiles Manufacturing Co., the turbidity decreased from 48.6 NTU to 29.0 NTU, corresponding to a decrease of 40.3 %. The high BOD of the raw or untreated wastewater from Tema Lube Oil may be due to the fact that, that wastewater contained more settleable and other solids that are organic and were easily oxidized by micro-organisms producing that high BOD value. Generally, during the treatments of all the wastewaters, the turbidity values decreased and hence the resulting BOD values were lower than for the raw wastewaters of each industry.

The effect of aerobic conditions on $PO_4$-P reduction was not significant. The level in the wastewater from Tema Lube Oil dropped by 10.2 %, while the level in the wastewater from Pioneer Food Cannery reduced by a percentage of 21.5 and for the Ghana Textiles Manufacturing Co. wastewater, a decrease of 8.37 % was observed. The generally low reduction observed for all samples, indicated that aerobic treatment is not a very suitable method for $PO_4$-P reduction. This is because, nutrient salts in the form of nitrogen and phosphorus salts are reduced only to a small extent by aerobic treatment which is a biological method of wastewater treatment, just like anaerobic treatment.[13] The biological processes remove barely 20 – 30 percent of total phosphate present in a wastewater and this is used in the growth of algae.

The processes involved in this reduction are biochemical, hence the extent of reduction depends on the presence of the right microbes, and other nutrients that are necessary for the incorporation of the phosphate by the microbes into cell material, thus removing them from the wastewater. The low levels of phosphate reduction may therefore be attributed to either a low concentration of the right micro-organisms that utilise orthophosphate as nutrients or the absence of some other nutrients that are necessary for its incorporation.

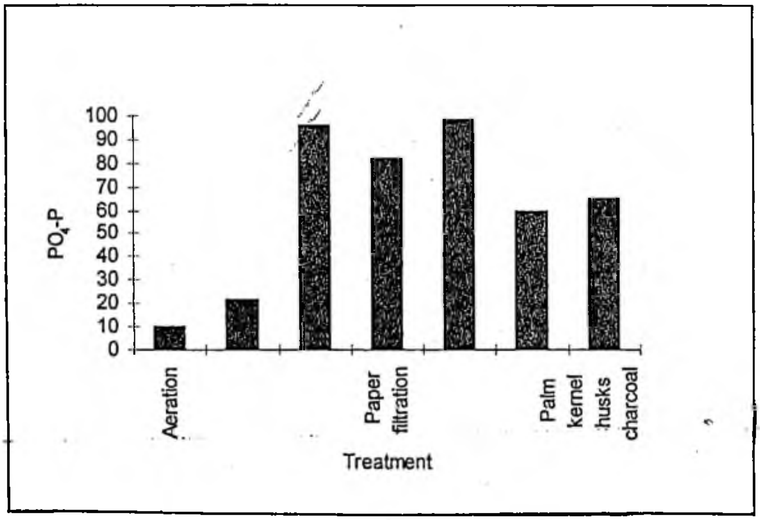

Fig. 34 - % Change of $PO_4$-P with Treatment for TLO

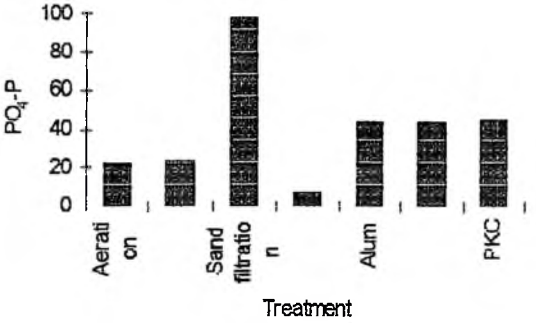

Fig. 35 - % Change of $PO_4$-P with Treatment for PFC

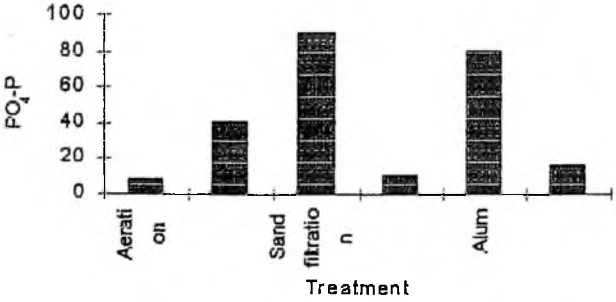

Fig. 36 - % Change of $PO_4$-P with Treatment for GTMC

Nitrate ($NO_3$-N) reduction was highest for Tema Lube Oil and was 60.00 %, from 0.0055 mg/L to 0.0022 mg/L. For Pioneer Food Cannery, there was no change and for Ghana Textiles Manufacturing, there was rather an increase of 18.7 %, from 0.71 mg/L to 0.81 mg/L. This could have resulted from the microbial breakdown of complex nitrogen-containing compounds into inorganic nitrates, in the wastewater from Ghana Textiles Manufacturing Co. which was measured by our method.[6] Thus, even though aerobic treatment will be a useful method for $NO_3$-N reduction in the wastewater from Tema Lube Oil, it will not be useful for the other two industries.

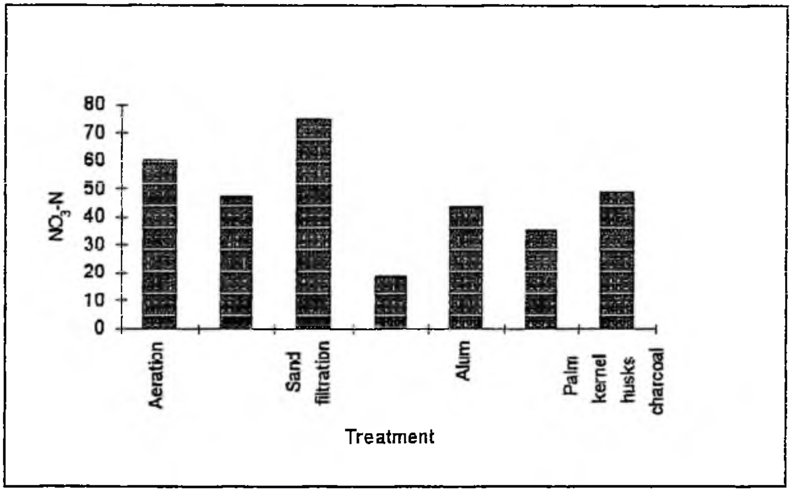

Fig. 37 - % Change of $NO_3$-N with Treatment for TLO

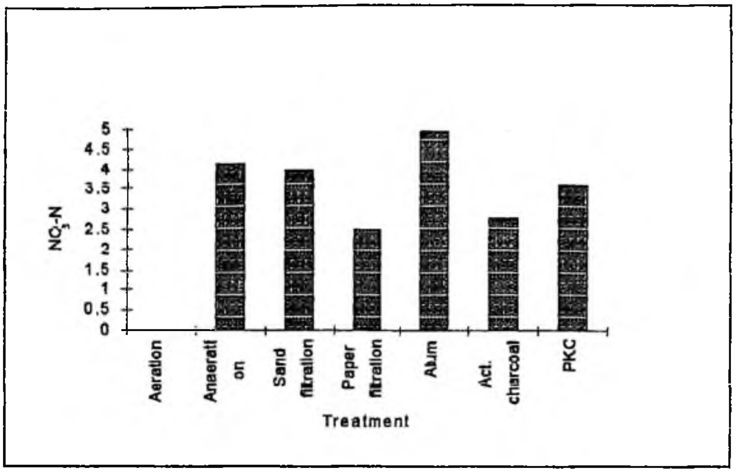

Fig. 38 - % Change of $NO_3$-N with Treatment for PFC

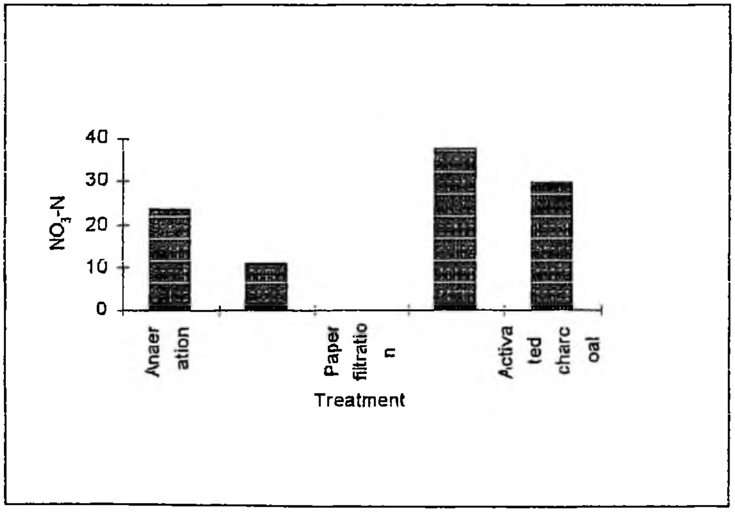

Fig. 39 - % Change of $NO_3$-N with Treatment for GTMC

Thus, even though aerobic treatment will be a useful method for $NO_3$-N reduction in the wastewater from Tema Lube Oil, it will not be useful for the other two industries. The usefulness of the method therefore can be said to be related to the type of effluent, which composition depends on the raw materials and the methods of production employed.

### 3.2.2 ANAEROBIC TREATMENT

Keeping the wastewaters under anaerobic conditions caused a reduction in almost all the parameters measured to some extent as shown in Tables 14 - 21. BOD reduction was 90.9 % for Tema Lube Oil, 35.3 % for Pioneer Food Cannery, and 42.1 % for Ghana Textiles Manufacturing Co. The Tema Lube Oil wastewater sampled contained domestic wastewater from their kitchen as well as their bathrooms, so it is more likely to be dosed with more of the micro-organisms that are necessary for the breakdown of the organic materials in the wastewaters. Also, unlike what obtains in Pioneer Food Cannery where the wastewaters are in open gutters, the sampling at Tema Lube Oil was done underground, where there is a semi-anaerobic environment that favours digestion. Although the treatment brought significant reduction in BOD, the value of 20.0 mg/L obtained for the treated wastewater from Tema Lube Oil, was below the EPA limit of 50.0 mg/L for wastewaters. Like the samples from the other two industries, it was above the WHO limit for potable water of $< 3.0$ mg/L. Hence, the treated waters cannot be used as potable water.

The $PO_4$-P reduction of 8.73% for Ghana Textiles Manufacturing was the lowest compared with 22.29% and 22.02% for Pioneer Food and Tema Lube Oil respectively. These values are in agreement with the up to 30 % reduction reported by Kemi[13] for biologically treated sewage.

A reduction of 47.3 % in the level of $NO_3$-N was obtained with anaerobic treatment applied to the wastewater from Tema Lube Oil. In the case of Pioneer Food Cannery Co., the reduction was only 4.08% and for Ghana Textiles Manufacturing Co., it increased by 18.7%. This increase of 18.7 % in the treated water from Ghana Textiles Manufacturing Co. was unexpected but could be due to nitrate formation by the microbial breakdown of complex nitrogen-containing compounds.[6] The nitrate concentrations for the raw, untreated samples were below the WHO accepted value of 10.0 mg/L but all the same, the nitrate levels of the treated samples were measured after the treatments, to find out the usefulness of the method in reducing the nitrate concentration in wastewaters.

The percentage turbidity decreases were 68.5, 54.5 and 9.47 for Tema Lube Oil, Pioneer Food and Ghana Textiles respectively, the same order as for the aerobic treatment. This is so because, during the treatments, a large amount of the suspended solids in the Tema Lube Oil wastewater settled easily and by the end of the seven days, most of the remaining amount had also settled, reducing the turbidity drastically. In the case of Pioneer Food Cannery, the colloidal wastewater which was bloody started coagulating and settling after about three to four days while for Ghana Textiles Manufacturing Co., after the seven days, the wastewater was still colloidal.

### 3.2.3 FILTRATION METHODS

In Table 7, the clay contents of the soils were established and this was necessary because, the clay component of soils is highly adsorbent as far as metallic ions are concerned. Table 8 is showing the decomposed fractions of the individual soils used, which is mainly organic. It was necessary to decompose the organic component of the soils, because it can be a source of organic pollution to the wastewaters, during their use to treat the wastewaters. With the filtration methods, the percentage reduction in the parameters measured was in many cases varied. In the case of sand filtration which proved to be the best, apart from the nitrate reduction which was very low for the wastewaters from Pioneer Food Cannery and Ghana Textiles Manufacturing Co., the BOD, $PO_4$-P, $NO_3$-N and turbidity reduction levels were significantly close and very high as seen in Tables 8, 9 and 10. Here, again, the turbidity of the raw and treated wastewaters increased with the BOD. In all instances, the new BOD values fell below the EPA allowed value of 50.0 mg/L but only the treated wastewater from Ghana Textiles Manufacturing had a BOD of 2.0 which was less than that of the WHO allowed maximum value of 3.0 mg/L. This treated water could therefore be used as potable water if disinfected either by chlorination, ozonation or ultra-violet irradiation.[17]

The $PO_4$-P reduction followed the order, Pioneer Food > Tema Lube Oil > Ghana Textiles Manufacturing with the respective percentage reductions of 97.0, 95.8 and 88.6. The order for turbidity reduction was Tema Lube Oil > Ghana Textiles Manufacturing Co. > Pioneer Food Cannery with per centage reductions of 97.8, 69.8 and 97.3% respectively.

Paper filtration was useful in the reduction of BOD and $PO_4$-P for Tema Lube Oil but not in nitrate reduction as seen in Tables 14 - 16. Again, the BOD decreased with the turbidity as in the other methods already discussed. The method can be useful in the reduction of turbidity in the wastewater from Pioneer Food Cannery and other wastewaters from the food industry that contain a large amount of suspended matter.

### 3.2.4 CHEMICAL COAGULATION (ALUM ADDITION)

This was another very useful treatment method in that most of the parameters were very much reduced in the wastewaters. In BOD reduction, the percentage reduction was 95.2 for Tema Lube Oil, 92.1 for Pioneer Food and 86.8 for Ghana Textiles Manufacturing Co. In general, the amount of suspended matter is greatly reduced by chemical precipitation which forms settleable flocs that are removable for example by simple decantation, hence they are not available for oxidation to increase the BOD of the mixtures after the treatment, resulting in low BOD values. The turbidity was also reduced very much by the method, which was in consonance with the low BOD values. The values were significantly reduced through a range of 97.3% in Tema Lube Oil to 63.0 % in Ghana Textiles Manufacturing.

The direct precipitation method used is very useful in the reduction of phosphorus too. $PO_4$-P levels were reduced very much but all the new values still exceeded the WHO value of less than 0.3 mg/L. Reduction in $NO_3$-N was generally low. Its values were already below the WHO allowed value of 10.0 mg/L, so it was not very necessary to monitor it, but there was the need to find out how the method affects the nitrate levels in wastewaters for possible use in future.

### 3.2.5 OTHER METHODS OF TREATMENT

Activated charcoal, palm kernel charcoal, Ekon clay and Elmina clay additions also gave interesting and significant results as shown in Tables 14 - 21. Like the charcoals, clay particles possess large surface area per unit mass, and have been reported to be highly adsorptive. The suspended solids are adsorbed on the clay particles which settle more rapidly with the suspended solids, thus making the solution clear, with a resulting BOD decrease.

The adsorptive properties of the clays and the activated charcoal as well as the other charcoals were clearly shown by their very effective reduction of the levels of the trace metals also.

### 3.2.6 TRACE METALS REDUCTION

The levels of the dissolved trace metals found in the wastewaters were not high but the fact that aquatic organisms are able to accumulate them and they can be introduced to man and cause problems made it necessary to find ways and means of their removal from the wastewaters.

Ni, Cu, Pb, Fe, Zn and Co in the untreated wastewater from Tema Lube Oil were 0.070 mg/L, 0.011 mg/L, 0.03 mg/L, 0.19 mg/L, 0.17 mg/L and below detection level in the same order as shown in Table 7. When the sample was treated under aerobic conditions for seven days, there was no change in the level of Cu which was fortunately already below both the EPA and WHO allowed values of 1.0 mg/L for wastewater and 1.0 mg/L for drinking water respectively. The levels of other metals decreased in some cases while in some they increased. Fe and Pb were below detection limit after the treatment. Before the treatment, Pb with a concentration of 0.03 in the untreated wastewater was below both the respective EPA and WHO limits of 0.1 and 0.05 mg/L but Fe with a concentration of 0.19 mg/L in the untreated water was above the WHO value of 0.05 mg/L. After treatment, the Fe concentration was below detection level. Ni decreased from 0.070 to 0.065 mg/L, which is quite insignificant. In the anaerobically treated sample, Zn decreased to 0.09 mg/L from 0.17 mg/L whilst Cu, Fe, Ni and Pb fell below detection level.

When sand filtered, Cu, Ni and Fe were not detected after the treatment. Zn decreased to 0.11 mg/L from 0.17 mg/L. Pb however, increased significantly from 0.03 mg/L to 0.11 mg/L. This could not be easily be accounted for. On treatment with the chemical coagulant (alum), the concentration of Ni increased to 0.130 mg/L from 0.070 mg/L, an increase of about 50% and Fe also went up to 1.31 mg/L from 0.19 mg/L. This could be due to interferences as a result of impurities in the alum used. Cu and Pb were however not detected.

Three other methods, paper filtration, activated charcoal and palm kernel husks charcoal treatments made significant reductions in the levels of all metals measured. Paper filtration reduced Cu, Fe and Pb to levels below detection limits whilst Zn decreased from 0.17 mg/L to 0.08 mg/L which was below the WHO allowed value for drinking water of 0.10 mg/L. Ni was reduced to 0.026 mg/L. In the case of activated charcoal, apart from Ni and Zn, the remaining metals were reduced to levels below detection limits, Zn decreased from 0.17 mg/L to 0.08 mg/L and Ni concentration was virtually the same, only reducing to 0.062 mg/L from 0.070 mg/L. With the exception of Zn which was detected to have decreased from 0.17 mg/L to 0.11 mg/L, the levels of the remaining metals measured were below the detection level after the use of palm kernel husks charcoal for treatment. This showed a good performance of the material in the treatment of these wastewaters.

As shown in Table 18, soil treatment seemed to have no effect on Zn but almost all the soils reduced the levels of the other trace metals, such that they were even not detected in the treated waters. This is expected, since the soils act as adsorbent and cation exchanger, adsorbing and exchanging some metals for others on their surfaces. But generally, Pb and Cu tend to be adsorbed most strongly and Zn and Cd are usually held more weakly so they are more labile and hence can remain in the treated wastewater.[26] This was exactly what was observed as far as Pb and Zinc were concerned. In an article in 'The State of the Environment in Nigeria[11], some of the water quality parameters measured for partially treated water from the WEMABOD Treatment Plant in Nigeria actually showed higher values than for the untreated wastewater. Here, treatment involved the addition of alum to the incoming wastewater from the factories and subsequent discharge without any sedimentation.

# CHAPTER FOUR

# CONCLUSION

## 4.1 INDUSTRIAL WASTEWATER EFFLUENTS AND POLLUTION

The levels of all the parameters measured showed that all the wastewaters from the industries were polluting to some extent. It can be concluded that the wastewater of TOR is a major source of dissolved salts, having a very high conductivity. It also contained a large amount of dissolved solids as a result of the sea-water used in the cooling process which is then discharged into the Chemu Lagoon.[60] Wastewaters from the textiles industries contained large amounts of total suspended solids (TSS) and total dissolved solids (TDS) as well as basic materials, as indicated by the high pH values. They also had high BOD and COD values in addition to intense colours.

The agro-based industries were particularly polluting in biochemical oxygen demand (BOD) and chemical oxygen demand (COD) and had low dissolved oxygen (DO). They also contained appreciable concentrations of nutrients like orthophosphates and nitrates which could encourage the growth of micro-organisms resulting in a secondary BOD load.

The levels of almost all the measured parameters exceeded the EPA limits or guidelines, a clear indication that the industrial wastewaters are potentially polluting.

Generally, it can be concluded that the wastewaters from the petroleum-based industries especially the wastewaters from TOR, were the most polluting in trace metals, followed by the chemical and paint industries and finally by the agro-based industries. Generally, the levels of trace metals were not high but considering the fact that even in small concentrations they are toxic and also that aquatic organisms are able to bioaccumulate them, they should be a source of concern.

No healthy biological life can exist in a stream with high BOD, pH, poor transparency, no dissolved oxygen and a high temperature.[77] and it is not surprising that water bodies like Chemu and Korle Lagoons have degenerated into the state in which they are today. Even with a dilution factor of 8, the industrial effluents could contribute significantly to pollution of the rivers, lagoons and the sea. Industrial effluents and domestic wastes disposal will continue to pose problems to mankind as long as increased industrial activity and human aggregation around the industrial areas are concerned. Wastewater disposal does not only affect rivers, lakes and other water bodies, but it also has an effect on land, which we depend on for our food.

## 4.2 RECOVERY OF USEFUL WATER FROM INDUSTRIAL WASTEWATER EFFLUENTS

Of the six methods investigated in the treatment of wastewaters from Tema Lube Oil Co., Pioneer Food Cannery Co. Ltd. and Ghana Textiles Manufacturing Co., sand filtration stood out as the single best method of treatment. It proved to be the singular, most effective treatment method which, was quite useful in reducing the pollution parameters from all the three industries, even to levels below the maximum limits. It was found out to be particularly useful in the case of PFC, where the experiment showed that, the method can be employed effectively and cheaply in treating not only their wastewaters, but those from other agro-based industries to produce water of sufficiently good quality for re-use for other acivities like crop and animal farming or for disposal into the environment. Chemical coagulation, done by alum addition, also showed some potentiality, but the addition of alum increased the pH and conductivity of the wastewaters, so the method has to be used with a lot of caution, with the end use of the refined water in mind. Apart for paper filtration, which was found to be the least effective method, the rest of the methods tried were found to be useful in the reduction of individual parameters in specific wastewaters.

Sand filtration, having been identified and singled out as a comparatively cheap and effective method of wastewater treatment, however have some limitations to its use, because of the waste sand that will be produced. It is therefore the wish of the workers that more work will be done to estimate the amount of waste sand that will be generated annually in the event of the large-scale employment of this method in wastewater treatment to find out probable and appropriate uses.

## 4.3 RECOMMENDATIONS

Existing factories should be encouraged to acquire suitable treatment plants whilst new ones should be sited so that effluent disposal is possible without nuisance and damage to the potable water bodies. Towards this end, the establishment of industrial estates should be promoted so that the industries collectively can put together infrastructure for treatment of wastes including wastewaters to make it cheaper. Also, some of the pollution problems will need to be tackled at their source, that is pollution problems should be considered at the early stages of planning human settlements and industrial activities. Pollution from industrial and other human activities must be brought under control before some success can be achieved in reclamation or restoration of many rivers and other water bodies. With concerted effort, this can be achieved. Raw materials and the methods of production could also be chosen in such a way that, the volume of wastes including wastewaters is not only reduced but the toxicity is also reduced.

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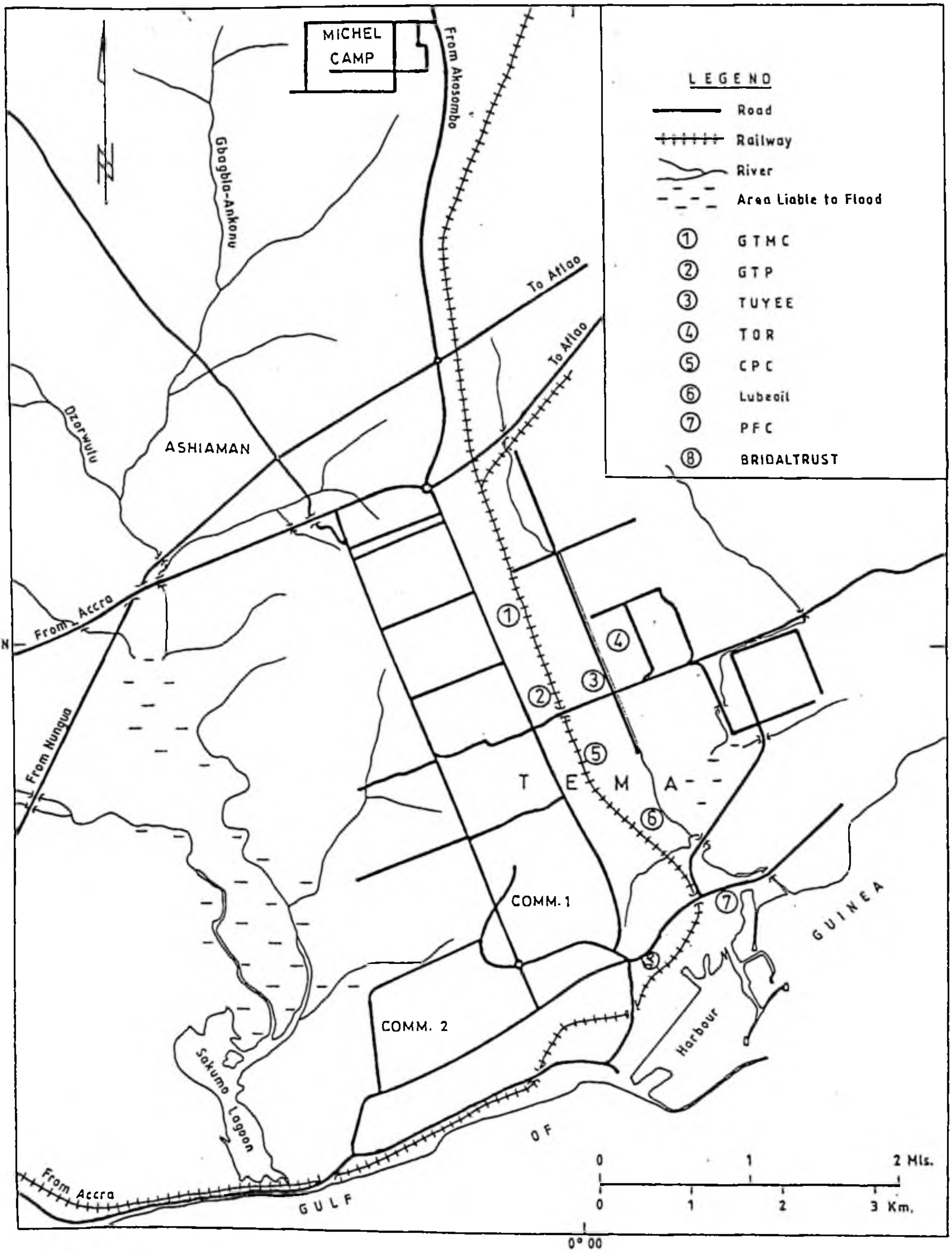
# APPENDIX I

## Map of Tema showing Industries sampled



# APPENDIX II

## CALIBRATION CURVES FOR SOME PARAMETERS

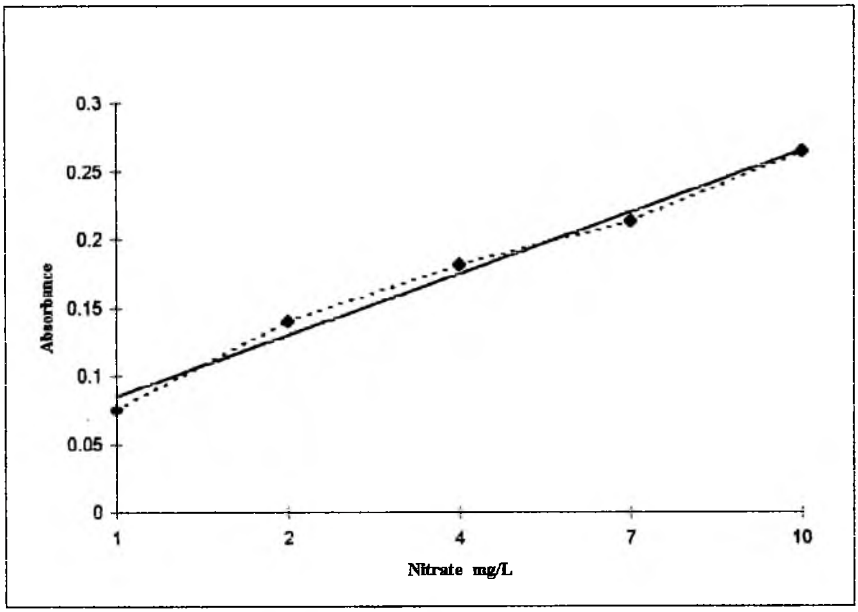


Fig. 40: CALIBRATION CURVE FOR THE DETERMINATION OF NITRATE

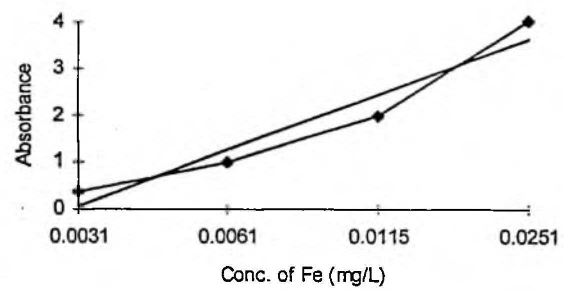


Fig. 41: CALLIBRATION CURVE FOR IRON (Fe)

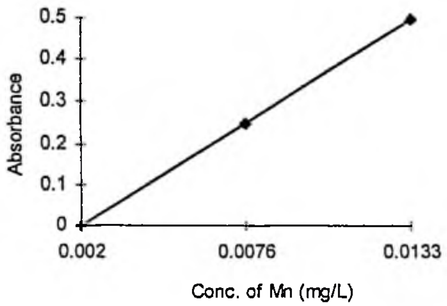


Fig. 42: CALLIBRATION CURVE FOR MANGANESE

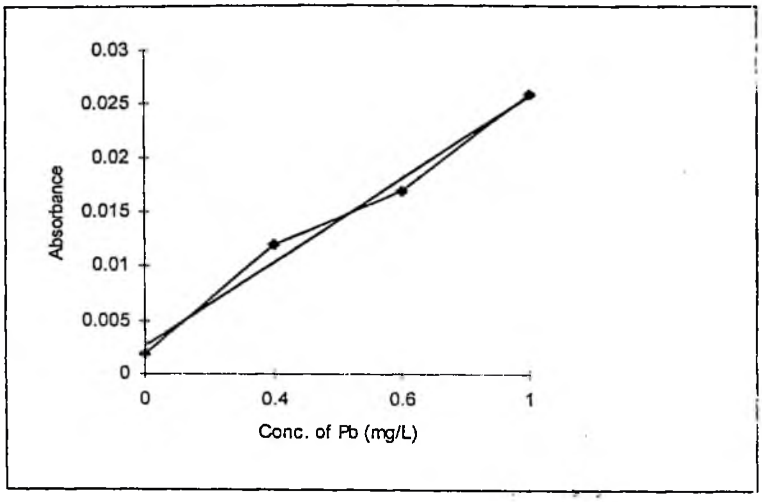


Fig. 45: CALLIBRATION CURVE FOR LEAD

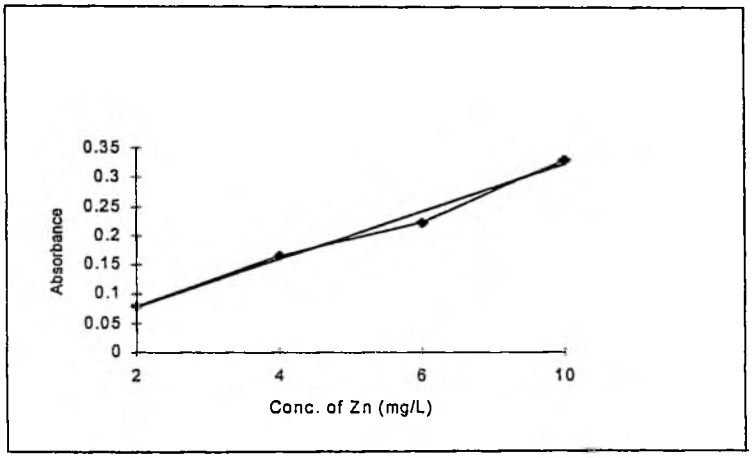


Fig. 46: CALLIBRATION CURVE FOR ZINC

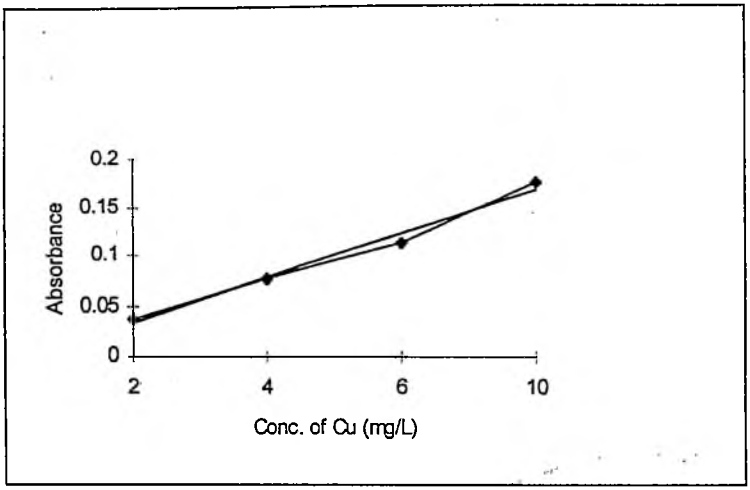


Fig. 43: CALLIBRATION CURVE FOR COPPER

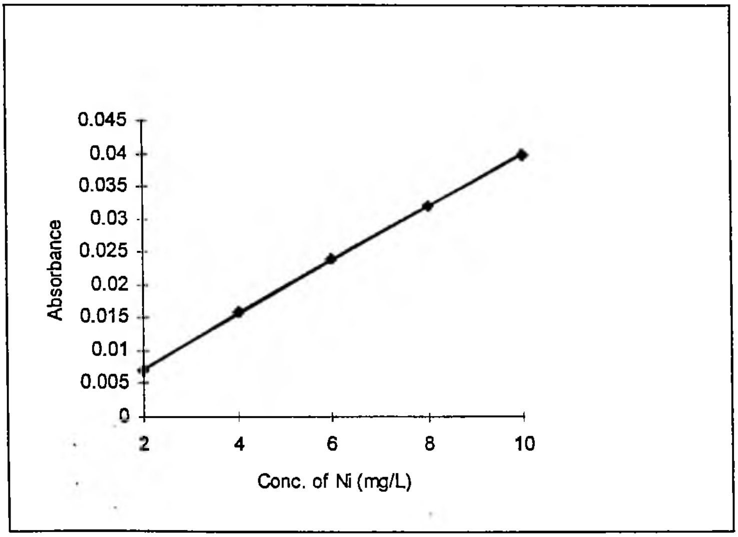


Fig. 44: CALLIBRATION CURVE FOR NICKEL

# APPENDIX III

## GRAPHICAL PRESENTATION OF THE VARIOUS PARAMETERS IN THE INDUSTRIAL WASTEWATERS

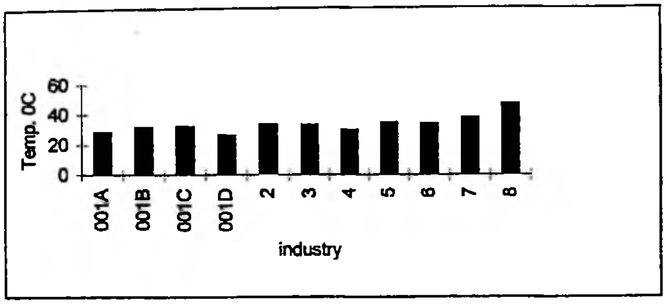


Fig. 2

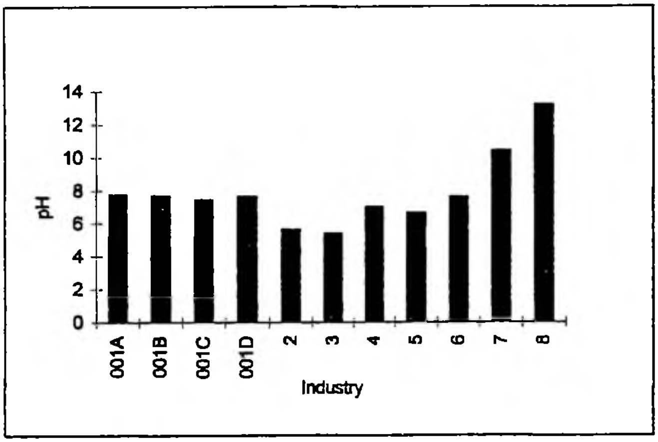


Fig. 3

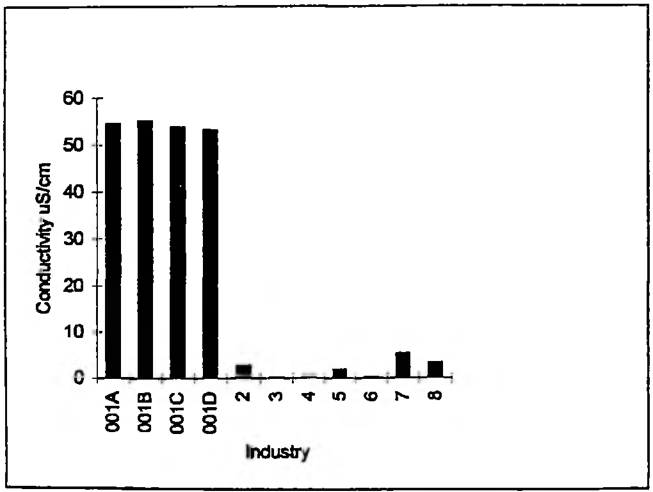


Fig. 4

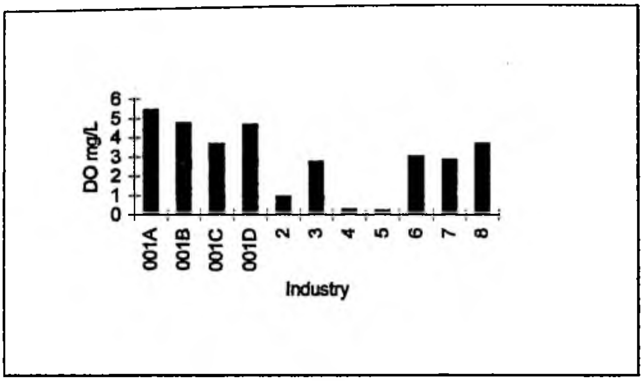


Fig. 5

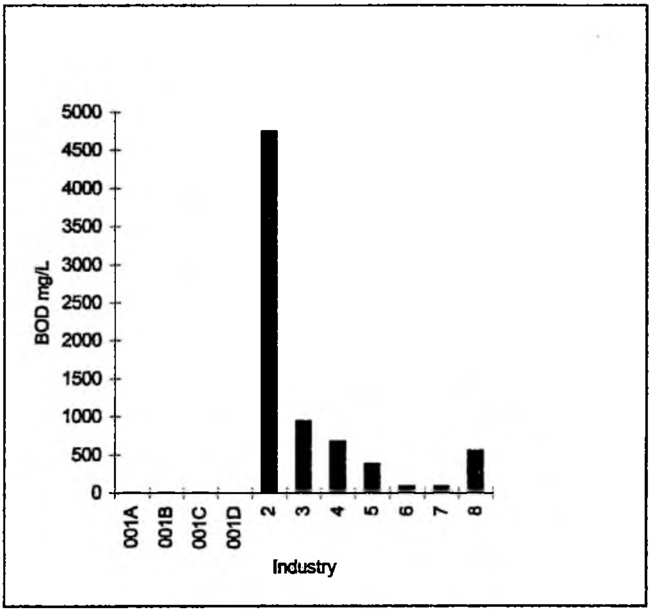


Fig. 6

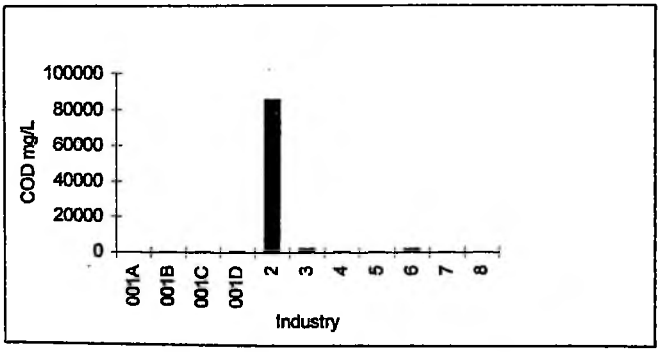


Fig. 7

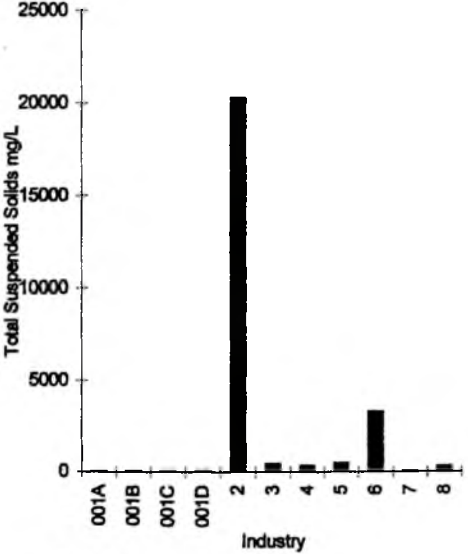

Total Suspended Solids mg/L
25000
20000
15000
10000
5000
0
001A
001B
001C
001D
2
3
4
5
6
7
8
Industry

Fig. 9

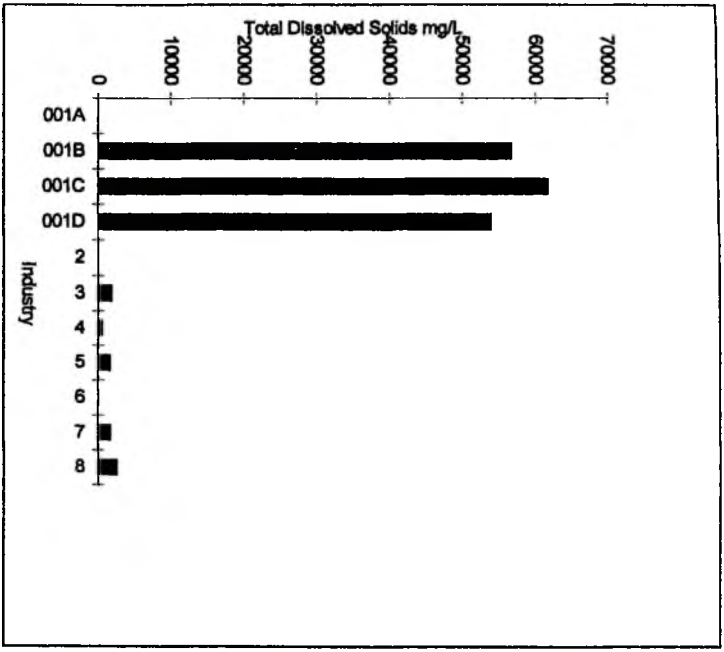

Total Dissolved Solids mg/L
0
10000
20000
30000
40000
50000
60000
70000
Industry
001A
001B
001C
001D
2
3
4
5
6
7
8

Fig. 8

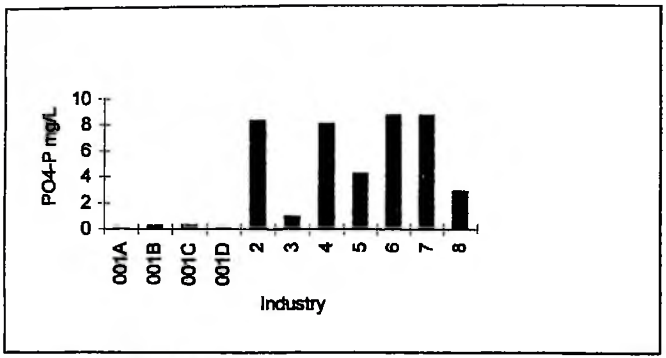


Fig. 10

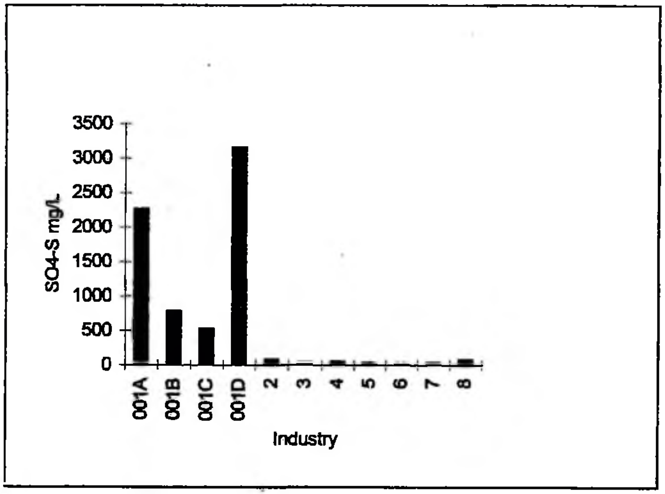


Fig. 11

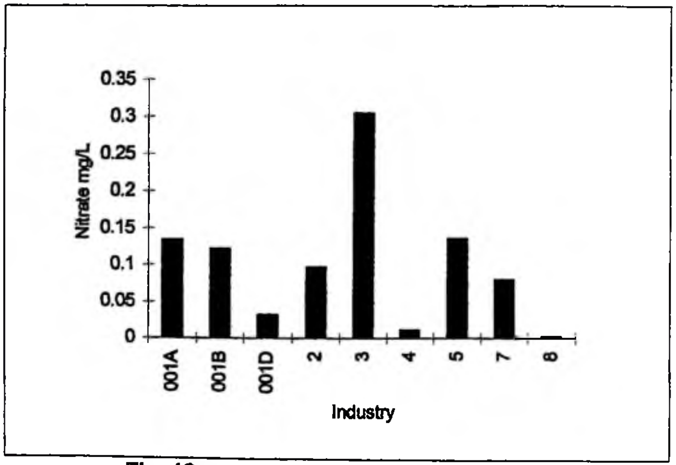


Fig. 12

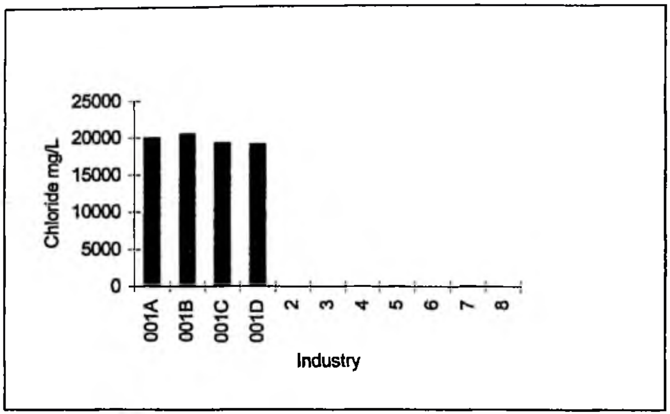


Fig. 13

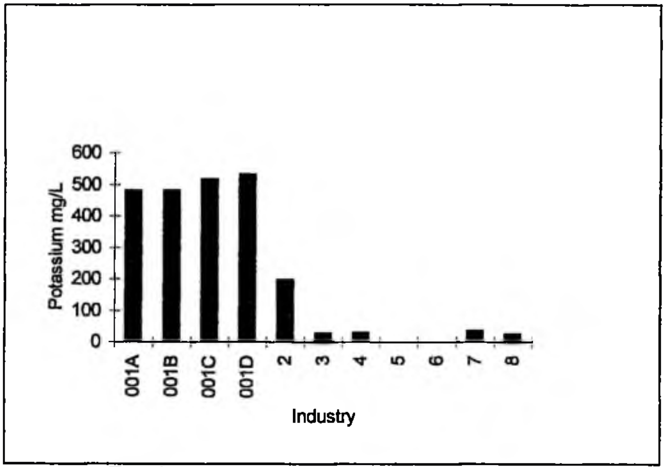


Fig. 14

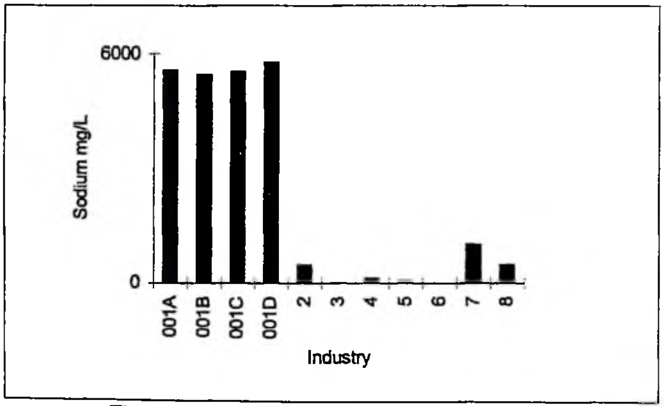


Fig. 15

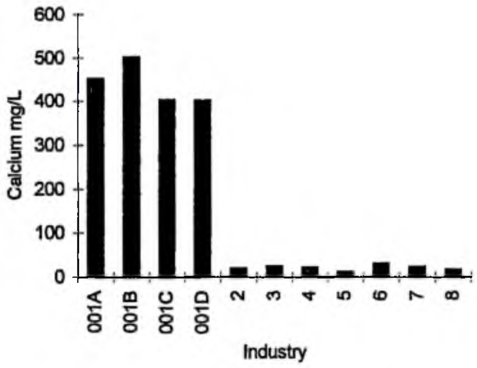

Calcium mg/L
600
500
400
300
200
100
0
001A
001B
001C
001D
2
3
4
5
6
7
8
Industry

Fig. 16

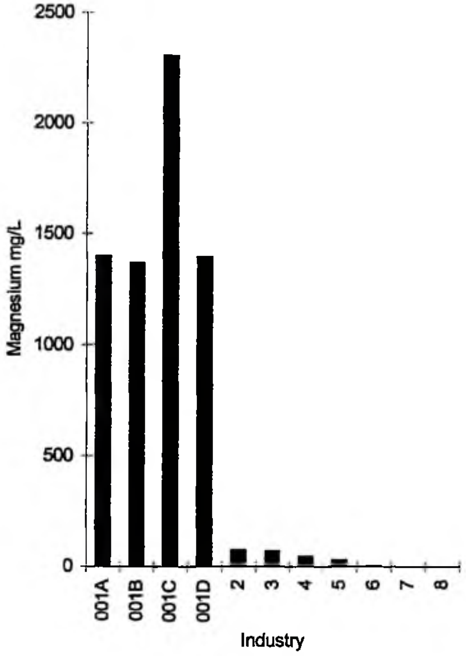

Magnesium mg/L
2500
2000
1500
1000
500
0
001A
001B
001C
001D
2
3
4
5
6
7
8
Industry

Fig. 17

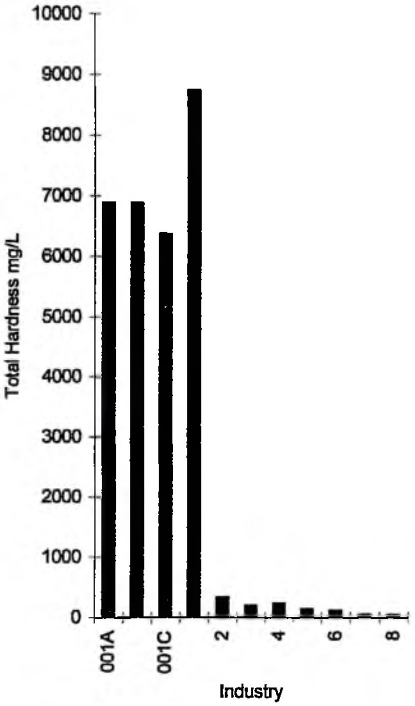

10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Total Hardness mg/L
001A
001C
2
4
6
8
Industry

Fig. 18

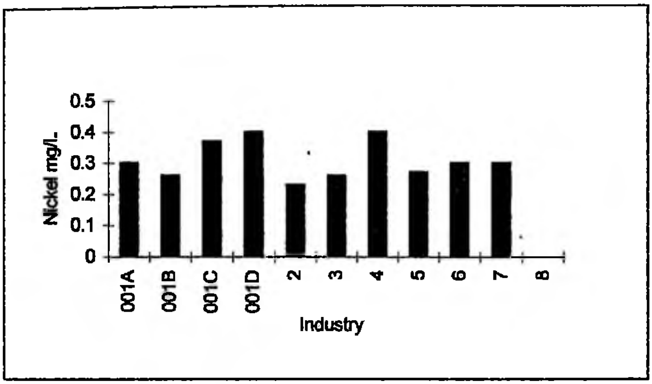


Fig. 19

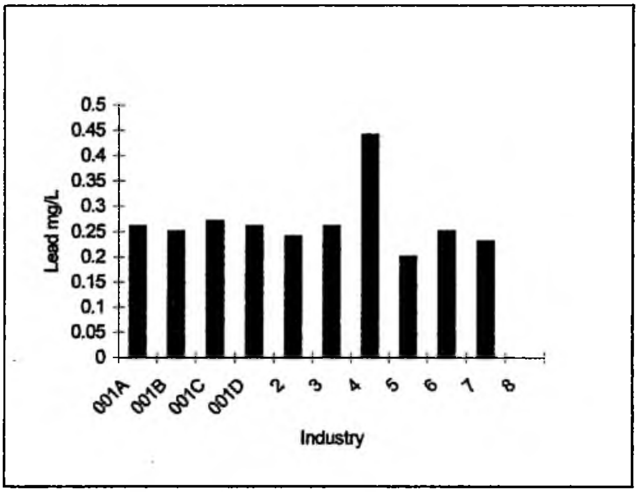


Fig. 20

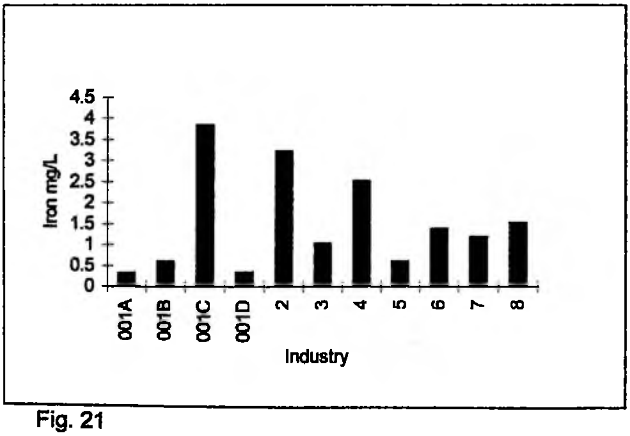


Fig. 21

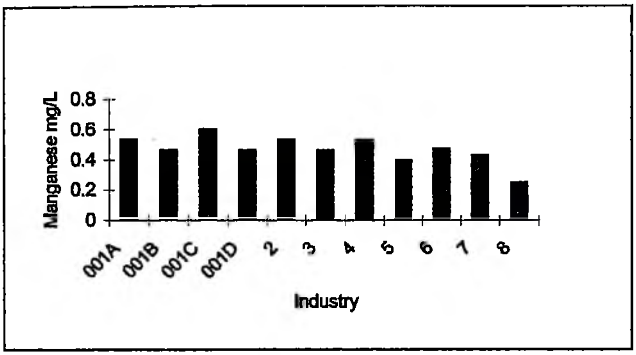


Fig. 22

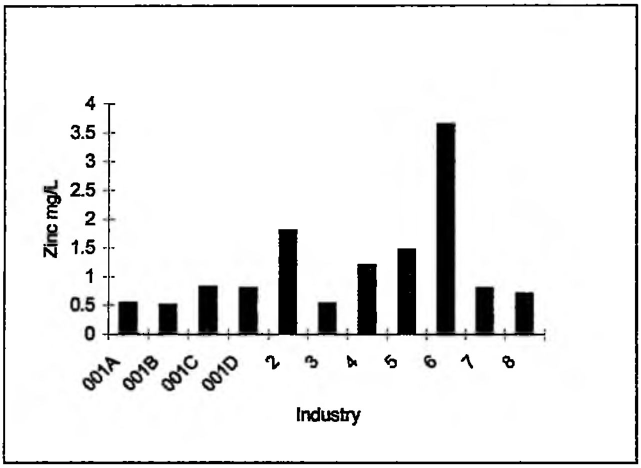


Fig. 23

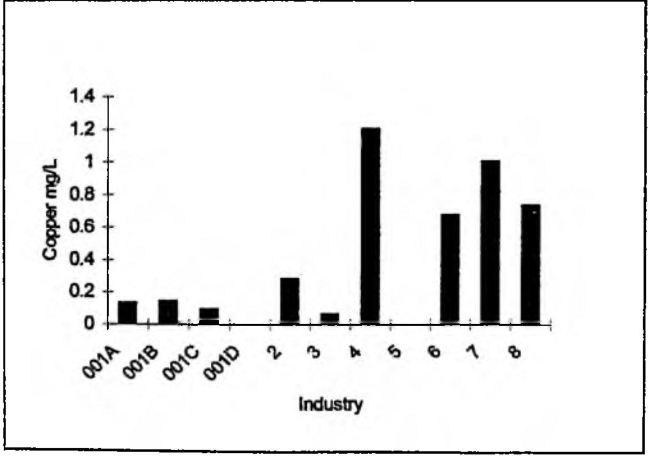


Fig. 24

Fig. 26

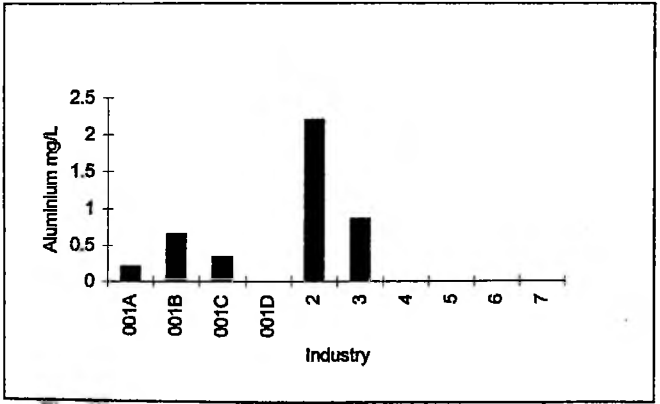

Aluminium mg/L
2.5
2
1.5
1
0.5
0
001A
001B
001C
001D
2
3
4
5
6
7
Industry

Fig. 27

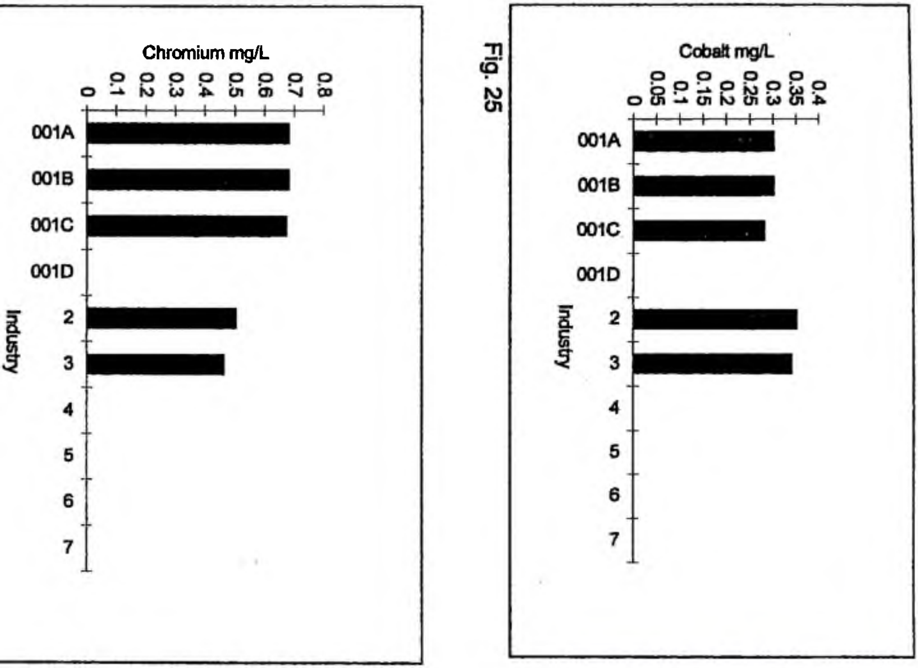

Chromium mg/L
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
001A
001B
001C
001D
2
3
4
5
6
7
Industry
Cobalt mg/L
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
001A
001B
001C
001D
2
3
4
5
6
7
Industry

Fig. 25

# APPENDIX IV

# PREPARATION OF REAGENTS

## Nitrate Determination

### Brucine-sulphanilic Acid

1 g of brucine sulphate.$7H_2O$ and 0.1 g sulphanilic acid were weighed and dissolved in 70 mL of deionized water. The resulting solution was stored in a dark bottle at 5 °C.

## DO Determination (Azide Modification Method)

### Manganese (II) sulphate Solution

5.00g of $MnSO_4.5H_2O$ was dissolved in a small volume of de-ionized water and the solution filtered. Some more water was used to wash the residue in the filter paper and finally, the solution was made up to 1 liter in a volumetric flask.

### Alkali – iodide - azide Solution

500g of NaOH and 135g of NaI were dissolved in a small volume of distilled water. 10g of sodium azide ($NaN_3$) dissolved in 40 mL of water was added and the mixed solutions made up to 1 liter with de-ionized water in a volumetric flask.

### Aqueous Starch Solution

5 00g of soluble starch was mixed with water into a smooth paste. This was poured into a 1 liter boiling water with constant stirring. The mixture was boiled for 1 minute and allowed to cool. 1.25g of salicylic acid was added as preservative.

### Sodium thiosulphate Solution (0.0250M)

6.3g $Na_2S_2O_3.5H_2O$ was dissolved in 1 liter of water. 1 mL of chloroform was used to stabilize the solution, which was stored in a brown bottle. This solution was diluted twice before being used for the titration.

**Potassium iodate (0.0250M)**

0.892g of potassium nitrate ($KNO_3$) previously dried at about 120$^0$C was dissolved in water and diluted to 1 liter. The 0.0125M thiosulphate solution was standardized with the 0.0250M iodate solution as follows. 10 mL of the iodate solution was pipeted into a conical flask containing 100 mL of water. 1 mL of the alkali-iodide-azide solution was added and then 2.0 mL $H_2SO_4$. The mixture was titrated with the thiosulphate solution, using starch indicator as the end point was approached.

## BOD Determination

**Alkaline-iodide-azide solution**

400 g of sodium hydroxide and 900 g of sodium iodide were weighed and 560 mL of water added. The solution was kept warm until all the iodide had dissolved. The mixture was cooled and diluted to one liter in a one liter graduated flask. 25 g of sodium azide was dissolved in enough water to give one liter of the solution. 300 mL of this azide solution was added to one liter of the iodide solution and thoroughly mixed to give the alkaline-iodide-azide solution.

**Dilution water**

The de-ionized water to be used in the preparation of the dilution water was saturated with dissolved oxygen by aerating with a supply of clean compressed air. The de-ionized water was at a temperature of 20 $^0$C. The desired volume of de-ionized water was placed in a plastic bottle that had been thoroughly cleaned with detergent and soaked in de-ionized water overnight. 1 mL each of phosphate buffer, magnesium sulphate($MgSO_4$), calcium chloride($CaCl_2$) and ferric chloride($FeCl_3$) solutions of 2M concentration was added to each liter of water and the contents of the bottle shaken to mix them well. The resulting water termed dilution water was used immediately to dilute the effluents when necessary.

## Calcium Determination

### EDTA (0.01M)

3.723g of disodium ethylenediaminetetraacetate dihydrate was weighed in a pre-dried crucible. The solid was dissolved in enough distilled water and diluted to 1 liter in a volumetric flask.

### Standard Calcium Solution

1.00g of calcium carbonate previously dried at 105 °C, was weighed and put in a 500 mL Erlenmeyer flask. Small volumes of 50% HCl were added through a funnel into the flask to dissolve the solid. 200 mL of water was added and the solution boiled until all $CO_2$ was expelled and cooled. Few drops of methyl red indicator were added and the colour of the solution adjusted to orange by adding small drops of either 50% HCl or 3M $NH_4OH$ solution. The solution was made up to 1 liter in a volumetric flask. It was used to standardize the EDTA solution using the buffer solution.

### NaOH Solution

40.0g of sodium hydroxide was dissolved in enough water in a 1 liter volumetric flask to give a Molar solution.

## Total Hardness Determination

### Buffer Solution

16.9g of $NH_4Cl$ was dissolved in 143 mL of conc. $NH_4OH$. 1.25 mg of the magnesium salt of EDTA was added and the resulting solution diluted to 250 mL with distilled water.

## Chloride Determination

### $AgNO_3$ Solution

2.395g of $AgNO_3$ was dissolved in distilled water and diluted to 1 liter in a volumetric flask. The solution was standardized with a standard NaCl solution prepared as outlined below.

### NaCl Solution for $AgNO_3$ Standardization

0.8241g of NaCl previously dried at 140 $^0$C was dissolved in enough distilled water and diluted to 1 liter in a volumetric flask. 1 mL of this solution is equivalent to 1.0 mg of $Cl^-$ ions.

### Potassium chromate Indicator

5.0g of potassium chromate ($K_2CrO_4$) was dissolved in 100 mL of water. Silver nitrate solution was added dropwise to produce a slight red precipitate of silver chromate and the solution was filtered. The filtrate is used as the indicator.

# APPENDIX V

## SAMPLE CALCULATIONS

### BIOCHEMICAL OXYGEN DEMAND

**Pioneer Food Cannery Company Limited**

$BOD_5$ = $(BOD_5 - BOD_1)$ x Dilution Factor

Titre value for $BOD_1$ = 7.90 mL

Titre value for $BOD_5$ = 3.30 mL

Dilution Factor = 100

$BOD_5$ = (7.90 mL - 3.30 mL) x 100

= 4600 mg/L

### CHEMICAL OXYGEN DEMAND

**Bridaltrust Paints Company Limited**

Dilution Factor = 4

Titre value for sample = 10. 00 mL

Titre value for blank = 25.40 mL

Conc. of $Fe(NH_4)SO_4$ = 0.0249 M

COD (mg/L) = 800 x (25.40 mL - 10. 00 mL) x 4 x 0.0249 M

= 1271.2 mg/L

## PHOSPHATE DETERMINATION ($PO_4$-P)

### Ghana Textiles Printing Limited

Dilution Factor = 10

UV Spectrophotometer reading = 0.0685 mg/L

Phosphate concentration = 0.0685 x 10 mg/L

= 0.685 mg/L

## FORMULAE FOR OTHER DETERMINATIONS

**Total Hardness (mg $CaCO_3$/L)**

$$\frac{\text{Average titre} \times 1000}{\text{Sample volume}}$$

**Calcium ($Ca^{2+}$) mg/L**

$$\frac{400.8 \times \text{Average titre}}{\text{Sample volume}}$$

**Calcium Hardness (mg $CaCO_3$/L)**

$$\frac{\text{Calcium ions (mg/L)}}{0.4}$$

**Magnesium Hardness (mg $CaCO_3$/L)**

Total Hardness (mg $CaCO_3$/L) - Calcium Hardness (mg $CaCO_3$/L)

**Magnesium ($Mg^{2+}$) mg/L**

Magnesium Hardness mg/L x 0.43