PHYSICOCHEMICAL CHARACTERISTICS AND AMENABILITY TO BENCH SCALE TREATMENTS OF SOME INDUSTRIAL EFFLUENTS AND SEDIMENTS IN LAGOS METROPOLIS

BY

CHIONYEDUA THERESA, ONWORDI

MATRIC. NUMBER: 66909

B.Sc (Industrial Chemistry), M.Sc (Analytical Chemistry), (Ibadan)

A Thesis in the Department of Chemistry

Submitted to the Faculty of Science in Partial Fulfilment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

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DEDICATION

This research work is dedicated to God the All Sufficient, and to unborn generations.

ABSTRACT

Untreated industrial effluents discharged into land and surface water are of great environmental concern. Previous studies on physicochemical characteristics of effluents and sediments from discharged points of various industrial sectors in Lagos metropolis are inadequate in scope, duration, chemical treatment options and estimated pollutant discharge load which are of importance in waste water management. This study was designed to investigate the physicochemical characteristics of effluents and sediments from industrial estates in Lagos metropolis, to estimate pollutant loads and determine appropriate chemical treatment options.

Effluents (75) and sediments (72) were sampled once in two months from the discharge points of textile, pharmaceutical, food and beverages, basic metals and paint industries from November 2006 to May 2008. Total Dissolved Solids (TDS), pH, alkalinity, total hardness, sulphate, phosphate, nitrate, chloride, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD)] and heavy metals were determined in the effluents according to APHA methods and compared with National Environmental Standards and Regulations Enforcement Agency (NESREA) limits. Organic carbon, pH and heavy metals were also analysed in the sediments. Multiple Linear Regression (MLR) was used to estimate organic load and eutrophication potential. Industrial effluent with the highest level of pollutant load was subjected to bench scale treatments using ferrous chloride, ferrous sulphate, Fenton's reagent, alum, and activated carbon separately. Efficiency of treatment was ascertained by determination of TDS and COD. The Pearson correlation at $p = 0.05$ was used to establish the significance between the levels of metals in the effluents and sediments..

Physicochemical characteristics (mg/L) of effluents from textile and pharmaceutical industries were 1160±890 and 630±260 for TDS, 316±280 and 230±97 for alkalinity, 60±32.and 53±44.for total hardness, 156±73 and 34±36 for sulphate, 1.0±0.3 and 0.7±0.6 for phosphate, 60.0±40.0 and 75±45 for nitrate, 65±19 and 61±40 for chloride, 1.8±1.7 and 1.3±1.2 for DO, 209±72 and 150±96 for BOD, 343±130 and 245±140 for COD, 0.7±0.3 and 0.5±0.2 for Zn, 1.5±1.0 and 0.3±1.1 for Cu, 2.5±0.3, 0.03±0.03 for Cr and corresponding pH was 10.6±1.1 and 5.5±1.2 respectively. Effluents from foods and beverages, basic metal and paint industries had lower levels of TDS, alkalinity, phosphate, and chloride. Nitrate, DO, BOD, and COD levels exceeded NESREA limits for all effluents. The pH and organic carbon ranged from 4.2-7.5 and 0.2-4.5% respectively for the sediments with the levels (µg/g) of Zn, Cr and Cu ranged from 196-3270, 7-49 and 21-244 respectively. Metal levels in sediments were higher than in effluent. Significant correlations were observed for Zn (0.64) and Cr (0.75) between effluents and sediments. The linear regression coefficients for organic load and eutrophication modelling ranged from 0.638-0.999 and 0.301-0.999 respectively. Efficiency of treatment options for COD reduction was in the order: Fenton's reagent (90%) > ferrous chloride (87%) > ferrous sulphate (66%) > alum (61%) > activated carbon (47%) while significant TDS reduction was not achieved.

Industrial effluents and related sediments in Lagos metropolis were highly polluted. Applications of Fenton's reagent and ferrous chloride were the appropriate chemical treatment options for organic pollutants in textile effluent.

Keywords: Industrial effluent and sediment, Heavy metal pollution, Lagos metropolis, Pollutant discharge load.

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Chionyedua Theresa, ONWORDI
June, 2014.

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CERTIFICATION

I certify that this work was carried out by **Miss C. T. ONWORDI** in the Department of Chemistry, University of Ibadan.

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LIST OF ACRONYMS AND ABBREVIATIONS

AF	Anaerobic Filter
AFB	Anaerobic Fluidized Bed
API	Active Pharmaceutical Ingredient
BOD	Biochemical Oxygen Demand
CA	Correspondence Analysis
CF	Contamination Factor
COD	Chemical Oxygen Demand
DA	Discriminant Analysis
DO	Dissolved Oxygen
FA	Factor Analysis
FEPA	Federal Environmental Protection Agency
GPS	Global Positioning System
HCA	Hierarchical cluster analysis
HRT	Hydraulic Retention Time
I_{geo}	Geo-accumulation index
LASEPA	Lagos State Environmental Protection Agency
MBRs	Membrane Bioreactors
NA	Not Available
ND	Not Determined
NESREA	National Environmental Standards and Regulations Enforcement Agency
PAC	Poly-Aluminium Chloride
PAFS	Poly-Alumino-Iron Sulphate Coagulant
PAHs	Poly-Aromatic Hydrocarbons
PAS	Poly-Aluminium Sulphate
PC	Principal Component
PCA	Principal Component Analysis
PCBs	Polychlorinated Biphenyls
PFS	Poly-Ferric Sulphate
PLI	Pollution Load Index

POME	Palm Oil Mill Effluent
PZ	Paterson Zochonics
SBRs	Sequence Batch Reactors
SS	Suspended Solids
TDS	Total Dissolved Solid
TSS	Total Suspended Solid
UASB	Up-Flow Anaerobic Sludge Blanket
VOCs	Volatile Organic Compounds
VSS	Volatile Suspended Solid
WHO	World Health Organisation

CHAPTER ONE

INTRODUCTION

1.1 INDUSTRIAL POLLUTION AND THE ENVIRONMENT

Industrial pollution has been and continues to be a major factor causing the degradation of the environment around us, affecting the water we use, the air we breathe and the soil we live on. Amongst these, the pollution of water is arguably the most serious threat to current human welfare. Water is polluted not only by industries but also by households. Both industries and household wastewater contain chemicals and biological matter that impose high demands on the oxygen present in water. Polluted water thus contains low levels of dissolved oxygen as a result of the heavy Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) placed by industrial and household waste materials discharged into water bodies and water systems. In addition to low levels of dissolved oxygen in water, industrial wastes (effluents) also contain chemicals and metals that are directly harmful to human health and the ecosystem (Samarghandi *et al*., 2007; Adekunle and Eniola, 2008; Mahdieh and Amirhossein, 2009).

Environmental pollution due to increase of industrial activities are one of the most significant problems of the century. Pollution of soil and water may be derived from human activities such as industrial production, agriculture, burning of fossil fuels, mining and metallurgical processes and waste disposal (Guiliano *et al*., 2007). Industries which use large amounts of water in their processes include chemicals manufacturing, steel plants, metal processors, etc. Effluents and most products from industries create serious pollution to water bodies and soils (Baskaran *et al*., 2009).

Partially or untreated industrial effluents may contain high levels of pollutants which in water body systems cause increase in BOD, COD, Total Dissolved Solids (TDS), Total Suspended Solids (TSS), toxic metals such as Cd, Cr, Ni and Pb, and feacal coliform, and hence make such water unsuitable for drinking, irrigation, and aquatic life support. Industrial wastewaters impacts include high BOD from biodegradable wastes such as those from human sewage, pulp and paper industries, slaughter houses, tanneries and chemical industry (Emongor *et al*., 2005; Otokunefor and Obiukwu, 2005; Phiri *et al*., 2005).

1.1.1 Impact of Industrial Emission on Land

Soil physiochemical properties are adversely affected by high concentrations of heavy metals, rendering contaminated soils unsuitable for crop production (Udom *et al*., 2004; Hernandez-Allica *et al*., 2007). Metals can also be transported through soil water resulting into soil contamination and inhibiting growth of plants (Sharma *et al*., 2008). Soils contaminated with toxic metals from point sources are potential exposure routes for surrounding population (Hindwood *et al*., 2004; Carrizales *et al*., 2006; Pruvot *et al*., 2006). The heavy metals accumulate in the plant material grown in these soils, which ultimately enters the human body through the food chain directly or indirectly. For example, the leather processing industry discharges huge volumes of waste water to irrigate agricultural lands in some communities. This waste water contains some proteins released during enzymatic processing of leather, and contaminants such as salts and chromium, that negatively affect soil processes and crop production (Alvarez-Bernal *et al*., 2006). Continuous disposal of such partially treated effluents results in soil and groundwater pollution not only in the effluent irrigated lands, but also the surrounding farmlands, through leaching/percolation and run-off from the effluent irrigated land. Contamination of both soil and groundwater (shallow and deep aquifers) quality may usually be quite evident, since drinking water in such vicinities may turn brown due to the presence of lignin in affected areas (Sundari and Kanakarani, 2001).

1.1.2 Impacts of Industrial Effluents on Water Bodies

Worldwide, water bodies are the primary receptacles for disposal of waste, especially the effluents from industries that are near them. Industries turn out wastes which are peculiar in terms of type, volume and frequency. The effluents often have the capacity to alter the physical, chemical and biological characteristics of the receiving water body. The extent of discharge of domestic and industrial waste is such that rivers receiving untreated effluent cannot give dilution necessary for their survival as good quality water sources (Sangodoyin, 1991). Industrial effluents are a main source of direct and often continuous input of pollutants into aquatic ecosystems with long-term implications on ecosystem functioning including changes in food availability and an extreme threat to the self-regulating capacity of the biosphere. These industrial discharge or wastes include heavy metals, pesticides, polychlorinated biphenyls (PCBs), dioxins, poly-aromatic hydrocarbons (PAHs), petrochemicals, phenolic compounds and microorganisms (Botkin and Kelly, 1998; Vesiland *et al*., 1990; Fakayode, 2005; Nubi *et al*., 2008). The initial effect of waste is to degrade the physical quality of the water. Later biological degradation becomes evident in terms of number, variety and organization of the living organisms in the water (Gray, 1989).

Industrial wastes containing high concentration of microbial nutrients obviously promote an after growth of significantly high coliform types and other microbial forms. Some heavy metals contained in these effluents have been found to be carcinogenic while other chemicals equally present are poisonous depending on the dose and duration of exposure. Undoubtedly, wastewaters from industries and residential areas discharged into another environment without suitable treatment could disturb the ecological balance of such an environment (Botkin and Kelly, 1998).

According to Perry *et al*. (2007), nitrogen, phosphorus, or both, may cause aquatic biological productivity to increase, resulting in low dissolved oxygen and eutrophication of lakes, rivers, estuaries, and marine waters. Eutrophication affects the aesthetics of water bodies (lakes, rivers), and results in odour and appearance problems. Besides adding to nutrient-content of the water, addition of some forms of nitrogen and phosphorus will increase BOD and COD (Mahdieh and Amirhossein, 2009). Increased nitrogen levels adversely affect cold-water fish more than they do warm water fish. Accumulation of trace metals occur in upper sediment in aquatic environment by biological and geochemical mechanisms and become toxic to reproduction and lower species diversity (Praveena *et al*., 2007).

Textile industries wastes typically include high concentrations of caustic chemicals of high pH values, between 10.0 and 11.0. The net effect is a variation of the acidic or basic nature of the water bodies (Comprehensive Industry Document Series, 1998). The release of coloured effluents into water bodies by textile industries is undesirable, not only due to their colour, but also because many synthetic dyes and their breakdown products are toxic and/or mutagenic (Saratale *et al*., 2009; Ben-Younes *et al*., 2011).

The pollution effects of untreated wastewaters of the steel industry, if discharged into the receiving water bodies are: toxicity to aquatic life, reduction of Dissolved Oxygen (DO), silting due to suspended solids, taste and odour problems, temperature rise affecting the DO and aquatic life, and formation of oil slicks due to floating oil. Considerable quantities of suspended and colloidal matter in the discharged effluents reduce the penetration of sunlight. Suspended and colloidal matter can also smother bottom dwelling aquatic organisms, affecting the life of water bodies, and leading to heavy siltation which affects the flow. Untrapped oil and grease from the effluent lead to formation of ugly oil slicks and iridescent colour which cause poor aesthetics. Oil slicks also reduce the diffusion of oxygen from the atmosphere to water, thereby affecting self purification. Where steel plants are located on the coasts, wave action invariably brings back oil and grease to the shore and spoils the beaches (Comprehensive Industry Document Series, 1998). There is thus a challenge of providing water in adequate quantity and of required quality to minimize hazards to human health and conserve the water bodies and the environment.

1.1.3 Impacts of Industrial Emission on the Atmosphere

Air pollution is one of the most serious issues in urban areas, due to its adverse effects on human health. In developing countries, an estimated 0.5-1.0 million people die prematurely each year as a result of exposure to urban air pollution (Kojima, 2001).Air quality standards, established for the protection of human health and environment, are being exceeded by mega-cities (Lin *et al*., 2001). Limits and the requirements for improved critical levels for air pollutants in the European Union highlight the need for both extensive and intensive monitoring programs to determine long-term critical exposure levels for damages (Mills *et al*., 2000/2001).

Energy related activities (production, transformation and use) are the major air polluters for almost all air pollutants. Gaseous pollutants include sulphur dioxide, nitrogen oxides (NO_x), ozone, carbon monoxide, Volatile Organic Compounds (VOCs), hydrogen sulphide, hydrogen fluoride and various gaseous forms of metals. These pollutants are emitted from both mobile and stationary sources which include fossil fuel, fired power plants, smelters, industrial boilers, petroleum refineries, incinerators and manufacturing facilities (Yusuf *et al*., 2013).With that, industry emits a large portion of greenhouse gases and is the major emitter of SO_2. In1996, industrial sources contributed about 20%, 17% and 22% of SO_2, NO_x and CO_2 respectively, to total EU emissions of air pollutants (European Environment Agency, 2000), while in 2004 the manufacturing industry contributed 17% in particulate matter, 15% in ground-level ozone formation precursors and 14% in acidifying substances (European Environment Agency, 2007).The impacts of air pollution include chronic respiratory illness, cardiovascular defects, cancer and even loss of life. Other consequences of air pollution include corrosion to various materials which cause damage to cultural resources, acid rain, damage of crops and other vegetation, including damage to aesthetic values, and reduced visibility (Yusuf *et al*., 2013).

Industrial emissions contain VOCs which emanate from industrial activities of various industrial units, and the products associated with them. These industrial units include ceramic and tile, lime and cement, metal plating, refineries, slaughter houses, metal foundries, food industries, detergents, dry cleaning, dyeing industries, tanneries, dairies, oil mills, fisheries, hydrometallurgical processes, aluminium recycling, piggeries, poultry raising, breweries, cosmetics, canning industries, pharmaceuticals, wood processing units, paper mills, production of construction materials etc. VOCs are carbon-based compounds that have vapour pressures that make them prone to significantly vapourise and enter the atmosphere (USEPA, 2005; EU, 2005). Studies have shown that VOCs enter the human bloodstream through inhalation, ingestion and dermal penetration (ATSDR, 2001).

In the Niger Delta region of Nigeria, the operations of petroleum industries especially the upstream and downstream sectors as well as a variety of other anthropogenically related activities including biomass combustion, refuse burning and traffic emissions release a barrage of substances like volatile organics, oxides of carbon, nitrogen, sulphur, particulate matter, heavy metals and other toxics at levels that most times exceed both the national and international guidelines (Tawari and Abowei, 2012). Apart from compromising the quality of the atmosphere, air pollution in the region is observed to have local and regional effects. Such effects include acid rain, water pollution, soil pollution, and injuries to plants and wildlife. Air pollution also damages materials and artifacts (Tawari and Abowei, 2012).

1.2 POLLUTION FROM INDUSTRIAL EFFLUENTS IN LAGOS STATE

Lagos is the most populated city in Nigeria and the second largest in Africa (Fig 1.1). Lagos lies between longitude 2° 42’ E and 3° 42’ E and Latitude 6° 23’N and 6° 41’N, which is approximately 1,000 sq. km in size with a coastline of about 180km (Akinmoladun and Adejumo, 2011). About 22% of the total landmass is made up of a network of creeks, rivers and lagoons (Adewuyi and Adeleye, 2013). The soils are mostly hydromorphic, clayey and sandy. It contains over 70% of Nigeria’s manufacturing industries (Oketola and Osibanjo, 2007) with the highest level of estimated emission of 8000 tons of hazardous wastes per year, most of which is discharged directly into the Lagos lagoon and cuts across the southern

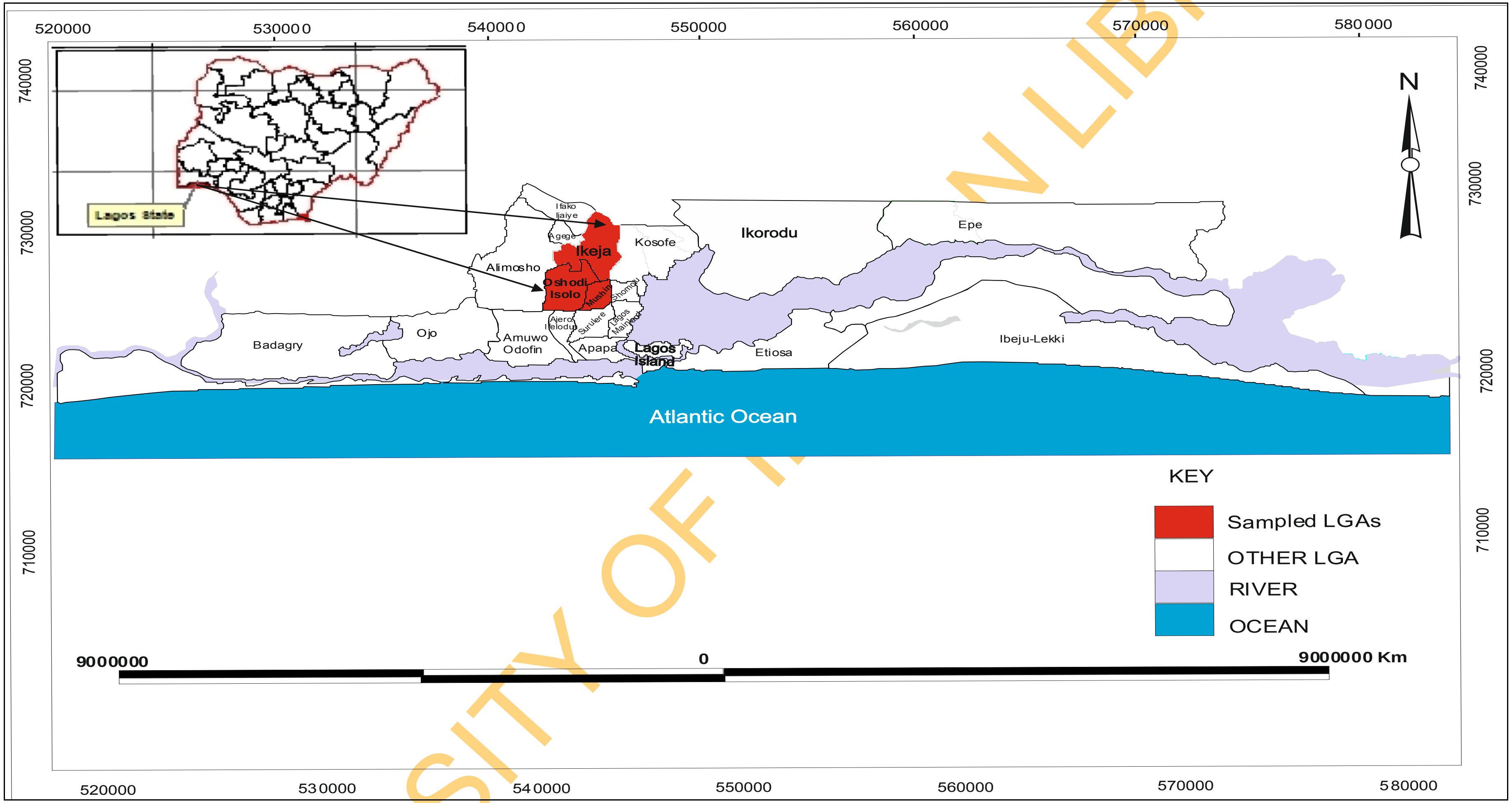

Fig 1.1: Map of Lagos State, showing Ikeja, Isolo, Mushin and other Local Government Areas.

part of the metropolis, linking the Atlantic Ocean (in the west and south), and Lekki Lagoon (in the east). It is about 6354.788sq km in area and 285 km in perimeter. The lagoon is generally shallow with a depth of between 0.3 and 3.2 m in most parts with the exception of some dredged parts, notably in the Lagos Harbour, where depth is greater than 10 m. The tidal range is 0.3-1.3 m. The lagoon provides places of abode and recreation, means of livelihood and transport, a dumpsite for residential and industrial discharge and a natural shock absorber to balance forces within the natural ecological system. The Lagos lagoon consists of three main segments namely the Lagos Harbour Segment, the Metropolitan and the Epe Division Segment (Ajao, 1996; IPEP, 2006; Adesalu *et al.,* 2010). Concentrations of some heavy metals at the site of sewage disposal in Lagos lagoon are: 0.07ppm Hg; 0.008ppm Pb; 0.66ppm Fe; 0.10ppm Cu and 0.03ppm Ni (Fodeke, 1979). It was reported that fish caught at the sites of industrial sewage discharge in the Lagos lagoon had high concentrations of heavy metals in them. These heavy metals are potentially dangerous to fish and man (FAO/WHO, 1972; Okoye, 1991). Adebayo *et al.* (2007) reported that there was decreasing concentration of metals (Fe, Cu, Cd, Mn, Cr, Zn, Mn, Pb, Cr, Cu, and Hg) from their source towards the Lagoon. Waters in the lagoon and ocean adjoining Lagos were found not to meet required standards and were thus are not fit for human consumption (Sangodoyin, 1995, Adebayo *et al*., 2007).

Lagos is home to some twenty- three (23) industrial estates (Table 1.1, Fig 1.2). It is the most developed area of the country with about a total of 5,000 ha of land occupied by the industrial estates (Soneye, 1997). The oldest industrial estate in Lagos is the Apapa Industrial Estate which occupies 100 hectares of land while the newest industrial estates are the Amuwo and Ikorodu/Odoguyan estates. The three largest industrial estates in terms of area occupied are Ikorodu/Ibese, Oregun and Ogba estates.

The lack of inadequate treatment of drinking water is one of the most critical crises in developing countries. Rivers, streams, wells, and borehole water are usually used as supplements for the scarce pipe borne water for drinking with little or no treatment. Drinking such water has led to the outbreak of epidemics such as cholera and other water related diseases on several occasions (United States Food and Drug Administration (USFDA), 1993; Frontiers, 1996; Umeh *et al*., 2004). The supply of water to several cities is limited, and in many cases, water supply is chronically insufficient for the inhabitants. Despite the

Table 1.1: List of industrial estates in Lagos State

Estate	**LGA**	**Year of Development**	**Area (hectares)**
Apapa	Apapa	1951	100
Mushin	Mushin	1957	30
Ijora	Apapa	1958	160
Badiya	Apapa	1958	15
Matori	Mushin	1958	120
Ikeja	Ikeja	1959	180
Agidingbin	Ikeja	1962	97
Ilupeju	Mushin	1966	110
Oshodi	Oshodi/Isolo	1968	120
Iganmu	Surulere	1968	80
Ogba	Ikeja	1969	414
Yaba/Oyadiran	Lagos Mainland	1970	20
Ilasamaja	Mushin	1971	60
Oregun	Ikeja	1971	500
Isolo	Oshodi/Isolo	1972	45
Gbagada	Somolu	1974	50
Ikorodu/Ibeshe	Ikorodu	1976	1580
Akowonjo	Alimosho	1976	50
Kirikiri	Apapa	1981	30
Surulere	Surulere	1981	20
Abesan/Ipaja	Alimisho	1981	100
Amuwo	Amuwo-Odofin	NA	NA
Ikorodu/odogiyan	Ikorodu	NA	NA

Source: Soneye (1997)

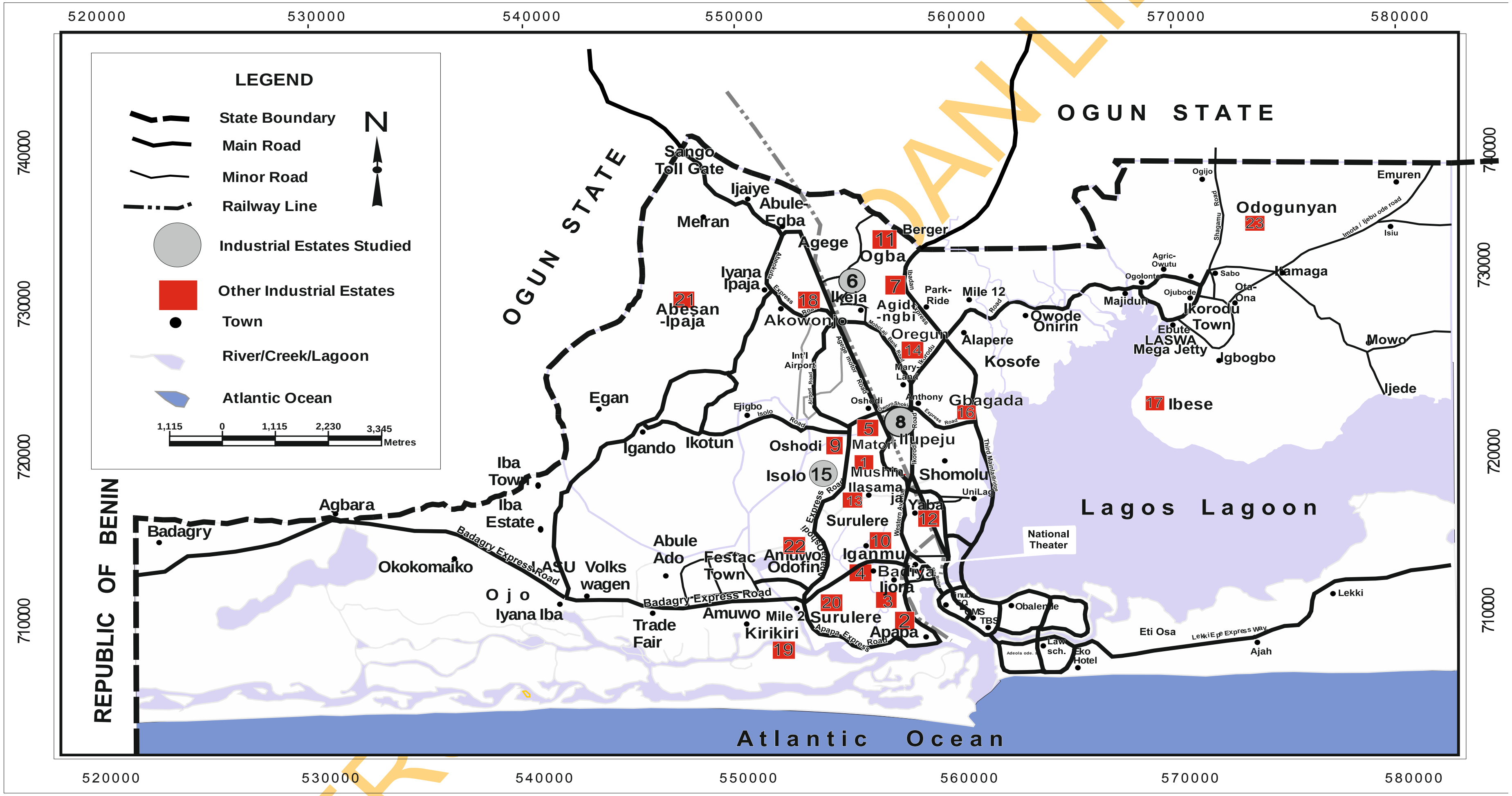

Figure 1.2: The spatial distribution of industrial estates within Lagos Metropolis.

inadequacy of water supply, the management and conservation of the available water bodies is generally poor. Industrial growth is fast increasing globally and so also is the water demand for industrial productions or processes. This has put more pressure on the limited available water resources. Water bodies are also constantly used as receptacles for the untreated waste water or poorly treated effluents accrued from industrial activities, which have rendered many water bodies unsuitable for both primary and/or secondary usage (Ogbeibu and Edutie, 2002).

These industrial estates were established and operated without proper consideration of their environmental impacts. As a result, rivers and streams received large volumes of industrial effluents daily, which frequently were beyond the auto in-stream recovery capacities. Liquid wastes are commonly discharged into sewers or rivers, which in many countries is subject to legislation governing treatment before discharge. In most states in Nigeria this legislation is not effectively enforced, and liquid wastes are discharged into water bodies or allowed to infiltrate into the soil. Where available indiscriminate disposal of liquid wastes pose a major pollution threat to both surface and groundwater.There are about 2000 industries in Lagos metropolis with industrial units such as chemical industries, metal industries, oil refineries, petrochemicals, tanneries, pharmaceuticals, textiles, etc of which many discharge their effluents into Shasa and Odo Iya Alaro streams in the densely populated and heavily industrialized Ikeja suburb (Oyeyiola *et al*., 2013). There are documented incidents of pollution caused by discharge of untreated industrial effluents to water bodies in Lagos metropolis (Novick, 1999; WHO, 2003). The water quality characteristics of the Shasa and Odo Iya Alaro streams, such as pH, BOD, turbidity, color, total suspended solid, oil and grease, pesticides and heavy metals as well as total coliform exceed the limits of WHO and Federal Environmental Protection Agency. All fresh water bodies in Lagos state and the Ogun river drain into the Lagos Lagoon. According to the industrial database research sponsored by the World Bank in 1996-1997, only seven (7) industries installed wastewater treatment facilities out of the 534 industries which answered to the questionnaires from the 2,000 industries in Lagos State (WES, 1997). A central treatment plant (the Ikeja Industrial Effluent treatment plant) was constructed by the Western Marketing Board, WEMABOD Estates Limited in 1965. It had the capacity to process 19,000 cubic metres of industrial waste water daily. It received wastewater from various industries, treated these and discharged into Shasa stream. A similar treatment plant for about twenty industries was constructed in Agbara Industrial Estate at Agbara between Lagos and Ogun States, which discharges treated water into the Owo river (Sowunmi, 2001). Wastewater from Iganmu and Apapa industrial estates are discharged directly into the Lagos Lagoon, Port Novo and Ebute Metta Creeks Apart from wastewater from Iganmu industrial estate, Nigerian Breweries which carries out physical and biological treatment (WES, 1997). It is noteworthy that the central wastewater treatment plant constructed by WEMABOD has remained dysfunctional and disused since the early 1980's; hence the wastewater that should have been treated at this facility is discharged untreated into a nearby stream through an underground sewer to Shasa stream. There are no central treatment plants in the other industrial estates, although a few industries partially treat their effluents whenever regulatory bodies propose visits to their premises. Meanwhile, monitoring by the regulatory body, Lagos State Environmental Protection Agency (LASEPA), is not effectively carried out. LASEPA's functions include the monitoring and control of the disposal of wastes in Lagos State, and advising the State government on all environmental management policies. The policies on environmental management in the various instruments of intervention are rarely enforced.

Previous studies on the characteristics of industrial effluents in Lagos metropolis have been very limited with respect to the class of industries studied, duration of studies and types of parameters investigated. In view of this, there has been the need to further comprehensively study the physicochemical characteristics of effluents from many more industries located in various industrial estates in Lagos.

1.3 AIMS AND OBJECTIVES

Environmental pollution associated with industrial is essential the problem of disposal of solid wastes and effluents (liquid or gaseous). All three types of wastes have the potential of ultimately polluting water. Polluted water, in addition to other effects, directly affects, soil not only in industrial areas but also in agricultural fields as well as the beds of rivers, thereby creating secondary effects. Farmers irrigate their gardens with water obtained from rivers and streams, which receive effluents from these industries. This practice has been on for a very long time, unabated. This research is therefore aimed at studying the degree of contamination of industrial effluents generated from three major industrial estates in Lagos metropolis and also to investigate the extent to which the effluents can be treated.

In view of the problem stated in section 1.2, the specific objectives of this study were as follows:

- To determine the levels of physicochemical parameters and heavy metals in industrial effluents from selected industries in Ikeja, Isolo and Ilupeju industrial estates.
- To determine physicochemical characteristics and heavy metals contents of sediments of some effluent channels.
- To determine physicochemical characteristics and heavy metals contents of soil samples besides the effluent channels, within the vicinities of the industries.
- To investigate the treatability of some of the effluents, using chemical methods.
- To apply the Multiple Linear Regression to generate models for estimating organic pollutant load (as COD) and eutrophication potentials (as phosphate) of the effluents.

CHAPTER TWO

LITERATURE REVIEW

2.1 OUALITY AND CHEMISTRY OF INDUSTRIAL EFFLUENTS

Production of wastes is a normal consequence of industrial activities. Unfortunately, our inability to anticipate or predict the types and magnitude of undesired consequences of unbridled release of effluents in our environment, coupled with the growth of industrialisation, have resulted in massive and destructive operations in our ecosystems. In most cases, effluents are discharged into rivers, estuaries, lagoons, or the sea without any form of treatment. Also, despite the treatment being employed by some industries, it is still impossible to remove all undesirable properties from effluents (Uaboi-Egbenni *et al*., 2009). The effluents of pharmaceutical, dyeing, printing, photography, textile and cosmetics industries contain dyes (McMullan *et al*., 2001). Pulp and paper industry produces a large quantity of wastewater of high organic strength (Moiseev *et al*., 2004; Satyawali *et al*., 2009). For most modern operations, approximately 60 m^3 of wastewater is generated for every tonne of paper produced (Thompson *et al*., 2001). Paper manufacturing processes include debarking, pulping, separation of pulp from cooking liquor, bleaching, stock preparation, and making the final paper products (Tezel *et al*., 2001). The pulping and bleaching processes produce the largest volume of wastewater whose composition is highly variable, depending on the implemented technologies (Mounteer *et al*., 2007; Ugurlu and Karaoglu, 2009). Paper mill effluents are loaded with organic matter with relatively high COD of about 800–4400 mg/L, BOD_5 of about 300–2800 mg-/L, and color of 1200–6500 color units (Buzzini *et al*., 2007; Singhal and Thakur, 2009; Sheldon *et al*., 2012). Paper mill waste also contain processed by-products such as extractives, carbohydrates, lignin and its derivatives, resin acids, sterols, and various chlorinated organic substances (Aaltonen *et al*., 2000; Kostamo *et al*., 2004; Leiviska *et al*., 2009).

Effluents from textile industries are a complex mixture of many polluting substances such as organo-chlorine based pesticides, heavy metals, pigments and dyes. Heavy metals have been associated with the textile effluents (Ekhaise and Anyansi 2005). Among the various types of organics present, colour-producing substances are the most difficult to remove. Colour contributes to increased BOD and COD. Azo dyes are used extensively in the textile and dyestuff industries; these dyes have a complex structure some of which are carcinogenic and mutagenic (Tripathi *et al*., 2007). Azo dyes are xenobiotics compounds characterized by the presence of one or more azo groups (–N=N–). They are considered a very important group of synthetic colourants. Of the annual world-wide production of dyes more than 50% are azo dyes, and around 2000 of them are used in the textile, leather, plastics, paper, cosmetics and foods industries (Stolz, 2001). Dispersed blue 79 (DB79) is one of the colorants with more application in the textile industry. It is used in the dyeing of polyester, nylon, diacetate and triacetate of cellulose as well as in acrylic fibers. The reductive cleavage of the azo linkage of the DB79 resulting in the formation of the amine 2-bromine-4,6-dinitroaniline (BDNA), which is toxic and mutagenic, and of the amine NN-disubstituted 1,4-diaminobencene.

Pharmaceuticals released into the environment are an important group of environmental pollutants (Jorgensen and Halling-Sorensen, 2000). Some studies have found pharmaceuticals in drinking water (Webb *et al*., 2003) and hospital wastewater (Suarez *et al*., 2009). Pharmaceutical industry wastewaters may contain organic solvents, catalysts, additants, reactants, intermediates, raw materials and Active Pharmaceutical Ingredients (APIs) (Sreekanth *et al*., 2009) which make them difficult to treat. The presence of toxic or recalcitrant substances in such wastewater results in lower COD removal efficiencies (Chelliapan *et al*., 2006). It has been estimated that up to half of the pharmaceutical wastewater generated worldwide is released without any treatment (Enick and Moore, 2007).

Paint making involves the mixture of pigment, binder, thinner and additives which when spread in a thin film forms a solid, adherent surface coating. The pigment gives the paint colour and hiding power; the binder acts as a film-former, which holds the pigment on the painted surface; the thinner brings the pigment-binder mixture to a suitable consistency for application, and the additives impart special properties such as rapid drying. The binder with the thinner is called the “vehicle” because together these two components carry the pigment to a surface. The pigment, the binder, and some additives (calcium carbonate, and aluminum silicate) make up the non-volatile matter, which becomes the dried paint film (Dey *et al*., 2004). There are two types of paints, water based paint and alkyd paint. Water based paint are also referred as “latex” paint. Water based paints can easily be apply to a surface, wash away with soap, dry faster, and have fewer odors than solvent paints. Alkyd paint is referred to as "oil-based" paint. Alkyd paints create more pollution than water based paint. The mixing of these different chemical compounds results in excessive discharge of some organic and inorganic substances to the environment (Morgan, 1982). Paint industry wastewaters are characterized by substantial organic matter, high salinity, sulphate and suspended solids contents (Aboulhassan *et al*., 2006). According to the World Health Organization (WHO 1984), the metals of importance in paint industrial wastewater are mercury, copper, chromium, zinc, iron and lead. Paint effluent is highly polluted in terms of COD, suspended solid (SS), lead, zinc, iron and copper

Industrial effluents from soap manufacturing industries are known to contain complex chemicals; e.g, most of which are very toxic and capable of destroying the microbial habitats in an adverse way. For example, characterisation of the composite wastewater from both soap and food processing plants indicated that the waste was highly contaminated with organic compounds as indicated by COD and BOD values (El-Gohary *el al*., 1987).

Effluents from food and beverages industries contributed significant pollution load to the Alaro river in Ibadan (Ipeaiyeda and Onianwa, 2011). The identified pollutants in the effluents were organic load, suspended solids, phosphate, nitrate and chloride which led to its significant pollution. The receipt of the effluents has rendered the river unwholesome for some beneficial purposes such as cooking, drinking, irrigation and aquatic life support (Ipeaiyeda and Onianwa, 2011). Brewery, the alcohol producing industry, is one of the major polluting industries. Brewing involves the making of fermented alcoholic beverages, such as beer and ale from cereal grains. Brewery wastes are composed mainly of liquor pressed from the wet grain and wash water from the various departments. After the distillation of the alcohol, the residue remaining is referred to as "distillery slops", or "still bottoms". The brewing industry consumes much water about 10 gallons of processed water / gallon of product. The BOD (260 mg/L); COD (854 mg/L); TSS (1050 mg/L) and Electrical Conductivity (3585 µmhos/cm) of the waste water are higher than the regulatory limits (Noorjahan and Jamuna, 2012).

2.1.1 Impact of Industrial Effluents on Water bodies

Water is essential to all forms of life and makes up 50-97% of the weight of all plants and animals and about 70% of human body (Buchholz, 1998). Water is also a vital resource for agriculture, manufacturing, transportation and many other human activities. Despite its importance, water is the most poorly managed resource in the world (Fakayode, 2005). Ground and surface waters can be contaminated by several sources. In farming areas, the routine application of agricultural fertilizers is the major source of pollutant (Altman and Parizek, 1995, Emongor *et al*., 2005). In urban areas, the careless disposal of industrial effluents and other wastes may contribute greatly to the poor quality of the water (Furtado *et al*., 1998, Chindah *et al*., 2004; Ugochukwu, 2004; Emongor *et al*., 2005). In recent years anthropogenic activity has introduced significant amounts of trace metals into aquatic environments (Puig *et al*., 1999). Anthropogenic water pollution is connected with sewage (industrial and communal), with lixiviation of chemical matter from dumping grounds of different waste materials, and with falls of atmospheric dust (Kabata-Pendias and Pendias, 1999). Industrial effluents from various industries like textile, dyestuffs, paper and pulp, distillery, olive oil mill and metal industries, etc. are the major contributors to water pollution as they create more subtle effects on behavior, reproduction or even survival of biotic communities (Tripathi *et al*., 2007). A study on the impact of industrial effluents on the water quality of a river in Nigeria (Fakayode, 2005) showed that the chemical parameters studied were above the allowable limits and also tended to accumulate downstream. The increasing demand on water arising from the fast growth of industries has put pressure on the limited water resources. While most people in urban cities of the developing countries have access to piped water, several others still rely on borehole and river water for domestic use. Most of the rivers in the urban areas of the developing world are the end points of effluents discharged from the industries. Industrial effluents, if not treated and properly controlled can also pollute ground water (Olayinka and Alo, 2004). Therefore, bore holes and rivers generally have poor quality water in affected areas. Since people use untreated waters from these sources, the result is continuous outbreaks of diseases such as cholera, bilharzia, diarrhoea and others (Umeh *et al*., 2004).

NEST (1991) studied the effect of thick black effluent from two breweries on Ikpoba River in Benin City, Nigeria and concluded that there was a decrease in dissolved oxygen, an increase in BOD, a massive increase in COD and an equally massive increase in total suspended solids, all of which have effect on the flora and fauna of aquatic life. Today in Nigeria, industrial effluents especially from textile mills have turned the water of Iya Alaro river and Shasha river permanently bluish-green as well as increased the pH, sodium compounds and lead contents (NEST, 1991). Industrial effluent characteristics provide basic information about the integrity of the aquatic habitat within such rivers and streams into which they are discharged. Most of these effluents pose inestimable harm to which the microbial entity is the most adversely affected (Barnes, 2004; Dallas, 2004). Most of the industrial effluents are known to contain significant concentrations of inorganic chemicals which affect not only the normal pH values but also lead to the hardness of the water (Ogunfowokan and Fakankun, 1998). These aquatic environments may put some components of the habitat to disadvantage. Industrial effluents from soap manufacturing industries are known to contain complex chemicals e.g most of which are very toxic and are capable of destroying the microbial habitats in an adverse way. For example, El-Gohary *et al*. (1987) presented the wastewater management of an industrial complex which produced different products, such as soap, perfume extract, macaroni, jam and juices. A continuous monitoring programme of effluents and characterisation of the composite wastewater from both the soap and brewery manufacturing processes indicated that the waste was highly contaminated with organic compounds as indicated by the high COD and BOD values. Moreover, effluent from the soap manufacturing plant contained significant concentrations of oil and grease amounting to 563 mg/L. Soap manufacturing effluent and the combined wastes discharged from the whole industrial complex were subjected to different treatment processes namely dissolved air flotation, chemical coagulation, sedimentation and biological treatment via a completely mixed activated sludge process (Agedengbe *et al*., 2003).

2.1.2 Impact of Industrial Effluent on Land.

Crowe *et al*. (2002) observed that exposure of oil sand effluents had an inhibitory effect on the germination of several plant species (tomato, clover, wheat, rye, pea, reed canary grass, loblolly pine). In addition, they observed that clover and tomato seeds' germination were most affected. Powell *et al*. (1996) also observed that fresh weights of seedlings were significantly reduced by treatment waters, while dry weights were generally unaffected when these plants were exposed to pollution stress. Caywela *et al*. (1996) and Zheng *et al*. (1998) found that seeds in iron-rich media germinated later than the control and showed physical deformities at the seedling stage. Soil kept moist with high sulphate waters (>1200 ppm) had a negative impact on the rate or percent of germination of barley and reed canary grass seeds, as compared to the controls (Golder Associates Ltd, 1997).

The problem of environmental pollution on account of essential industrial growth is in practical terms, the problem of disposal of industrial effluents. All three types of wastes (solid, liquid, and gaseous) have the potential of ultimately polluting water. Polluted water in addition to other effects, directly affects soil in industrial and agricultural areas, as well as the beds of rivers, thereby creating secondary sources of pollution (Barman *et al*., 2000; Kisku *et al*., 2000). Use of industrial effluent and sewage sludge on agricultural land has become a common practice in Nigeria as a result of which toxic metals (Pb, Hg, Zn, Cu, etc) can be transferred and concentrated into plant tissues from the soil. These metals have damaging effects on plants themselves and may become a health hazard to man and animals. Above certain concentrations and over a narrow range, the heavy metals become toxic (Babich *et al*., 1982). In addition to providing large quantities of water, some effluents contain considerable amount of essential nutrients which may prove beneficial for plants.

The bio-accumulation of heavy metals in different terrestrial biota was investigated in Kenting National Park, Taiwan and high concentrations of Cd, Hg, and Sn were found in snail, earthworm, crab, lizard, snake, and bat. Similarly, high level of Hg was found in invertebrates, amphibians and reptiles which revealed a strong influence from industrial effluents (Hsua *et al*., 2006)**.**

The effluents released from the sugar industry contain high degree of organic pollutants which has effect on aquatic and terrestrial ecosystems. The use of this industrial effluent and sewage sludge on agricultural land is a common practice in many places, especially Nigeria (Odjegba and Bamgbose 2012), as a result of which these organic pollutants can be transferred and get accumulated into plant tissues from the soil. These organic pollutants have damaging effects on the plants themselves and may become a health problem to man and animals (Ayyasamy *et al*., 2008). The effluents also alter the physicochemical characteristics, flora and fauna of receiving aquatic bodies. In addition, the sugar factory effluent discharged to the environment poses a serious health hazard to the rural and semi-urban populations that use stream and river water for agriculture and domestic purposes.

2.2 EFFLUENT TREATMENT

Control of pollution is one of the prime concerns of society today. With economic constraints on pollution control processes, affordable and effective methods have become a necessity. Industries have four possibilities for disposal of their wastewaters, namely:

- They may treat their wastewaters separately in an industrial wastewater treatment plant prior to discharge into a water course.
- They may discharge their wastewaters into municipal treatment plants for complete treatment.
- Their wastewaters can be pre-treated at the industrial wastewater treatment plant prior to discharge into the municipal sewerage system.
- Industrial wastewaters can be discharged directly into water course without any treatment (industries will prefer this method because of the economic advantage).

Treatment of industrial effluents could be achieved by biological methods, chemical methods and physical methods. Biological methods are those that involve living organisms using organic, or in some instances, inorganic, substances for food, completely changing their chemical and physical characteristics. The biological treatment of industrial effluents is achieved with the aid of microorganisms (Frank, 2001).

Chemical methods include chemical precipitation, chemical oxidation or reduction, formation of an insoluble gas followed by stripping, and other chemical reactions that involve exchanging or sharing electrons between atoms.

Physical treatment methods include sedimentation, flotation, filtering, stripping, ion exchange, adsorption, and other processes that accomplish removal of dissolved and undissolved substances without necessarily changing their chemical structures (Frank, 2001).

The chemical and physical methods of industrial effluent treatment processes remove organic pollutants at low level; they are highly selective to the range of pollutants removed and prohibitively expensive (Tripathi *et al*., 2007).

2.2.1 Biological Treatment Methods

Biological treatment methods use microorganisms, mostly bacteria, in the biochemical decomposition of wastewaters to stable end products. The biological or biochemical treatment, unlike other forms, is in a large scale and the widest spread method of treating sewage. The method is based on the biochemical oxidation of organic and inorganic substances due to the activity of microorganisms using impurities such as a nitrite substrate, and forming harmless oxidation products: water, CO_2, NO_3^- and SO_4^{2-} ions and also biochemical matter. The degree of decomposition of organic compounds in biological treatment is characterised by the ratio BOD/COD. The greater the biological oxidation of a given waste, the higher is this ratio (Nsi, 2007). In biochemical treatment of effluents, the numerous organisms used constitute bacteria. A wide range of bacteria has been recorded (Ugoji and Aboaba, 2004; Iyagba et al., 2008), but the dominant aerobic genera appear to be gram-ve rods; pseudomonas, achromobacter, alcaligens and flavobacterium. Fungi are normally outnumbered 8:1 by bacteria. Autotrophic bacteria tend to be more predominant in the lower layers of the biofilms with nitrosomonas oxidizing nitrite to nitrate (Christopher, 2002). Protozoa, according to Ajao *et al.* (2011) and algae, according to Laliberte *et al.* (1994), have also been implicated in the biological treatment of effluent from pharmaceutical companies. Generally, biological treatment methods can be divided into aerobic and anaerobic methods, based on availability of dissolved oxygen. Aerobic applications include activated sludge, sequence batch reactors and membrane batch reactors (LaPara *et al.*, 2002; Suman Raj and Anjaneyulu, 2005; Noble, 2006; Chang *et al.*, 2008 and Chen *et al.*, 2008). Anaerobic methods include anaerobic sludge reactors, anaerobic film reactors and anaerobic filters (Gangagni *et al.*, 2005; Enright *et al.*,2005; Chelliapan *et al.*, 2006; Oktem *et al.*, 2007; Sreekanth *et al.*, 2009). The advantages of anaerobic treatment over aerobic processes is its ability to deal with high strength wastewater, with lower energy inputs, sludge yield, nutrient requirements, operating cost, space requirement and improved biogas recovery.

2.2.1.1 Conventional activated sludge

Conventional activated sludge with a long hydraulic retention time (HRT) has historically been the method of choice for the treatment of pharmaceutical industry wastewater (El-Gohary and Abou-Elea, 1995; Oz *et al.*, 2004). It has a lower capital cost than more advanced treatment methods and a limited operational requirement; it is generally more environmentally friendly than chlorination. However, high energy consumption, the production of large amounts of sludge (Sreekanth *et al.*, 2009) and operational problems including colour, foaming and bulking in secondary clarifiers are associated with activated sludge plants (Oz *et al.*, 2004). Factors which affect the efficiency of activated sludge facilities for the treatment of pharmaceutical wastewater include HRT, temperature, pH, dissolved oxygen (DO), organic load, microbial community, presence of toxic or recalcitrant substances and the batch operation of pharmaceutical production facilities (LaPara *et al.*, 2001; LaPara *et al*., 2002; Suman Raj and Anjaneyulu, 2005). These variables require modification for adaptation to pharmaceutical industry wastewater.

2.2.1.2 Sequence batch reactors

A number of pilot scale studies were conducted using Sequence batch reactors (SBRs) and Membrane bioreactors (MBRs) in an attempt to improve the effectiveness of activated sludge treatment (Clara *et al*. 2005; Radjenovic *et al*. 2007). SBR is an activated sludge method of treatment in which separate tanks for aeration and sedimentation are not required and there is no sludge return. This type of process is ideal for use in small systems or when land is limited (Ileri *et al*., 2003). In one study, removal rates of 82 % BOD, 88 % COD, 96 % NH_3 and 98 % Suspended solids (SS) from domestic and pharmaceutical wastewater were achieved with a SBR operated for a 4 h aeration and a 60 min sedimentation period (Ileri *et al*., 2003). In another study, slightly lower removal efficiencies of between 63-69 % of COD levels were achieved using SBR technology (Aguado *et al*., 2008).

2.2.1.3 Membrane bioreactors (MBRs)

Membrane bioreactors (MBRs) are known to be effective for the removal of bulk organics and can replace traditional methods or operate in combination with conventional AS systems or as hybrid systems (Noble, 2006). The main advantages of MBRs over AS is that they require less space for operation (Yang *et al*., 2006), and can also treat variable wastewater compositions (Chang *et al*., 2008). High COD and BOD removal have been demonstrated in pharmaceutical production facilities (De Wever *et al*., 2007). For example, a 10 m^3 per day capacity MBR operated at a pharmaceutical facility in Taiwan, removed 95 % of COD and 99 % of BOD (Chang *et al*., 2008). However, complete removal of all APIs is rare (Helmig *et al*., 2007). While the MBR removed 17- α-estradiol, 17-β-estradiol, 17-α-dihydroequilin, trimegestone, estriol, medrogestone, norgestrel, and estradiol valerate to near and below the detection limits, estrone, ethinyl estradiol, and venlafaxine, a selective serotonin reuptake inhibitor (SSRI), were shown to be more resistant to the MBR treatment (Helmig *et al*., 2007). One explanation for this is that pharmaceutical compounds are generally smaller than the membrane pores and so only substances sorbed on particles are retained (Radjenovic *et al*., 2007). In order to remove the smaller compounds, membranes such as those used in reverse osmosis or nanofiltration are used. However, these are expensive, and limited in widespread use (Clara *et al*., 2005).

2.2.1.4 Anaerobic sludge reactors

Up-flow anaerobic sludge blanket (UASB) technology, normally referred to as UASB reactor, is a form of anaerobic digester that is used in the treatment of wastewater (Borja *et al*., 1994a). UASB was developed by (Lettinga *et al*., 1980) whereby this system has been successful in treating a wide range of industrial effluents including those with inhibitory compounds. The UASB reactor is a methanogenic (methane-producing) digester that evolved from the anaerobic clarigester. The underlying principle of the UASB operation is to have an aerobic sludge which exhibits good settling properties (Lettinga, 1995). So far, UASB has been applied for the treatment of potato wastewater (Kalyuzhnyi *et al*., 1998, Lettinga *et al*., 1980, Parawira *et al*., 2006); domestic wastewater (Barbosa and Sant'Anna, 1989; Behling *et al*., 1997); slaughterhouse wastewater (Sayed *et al*., 1984); Palm oil mill effluent (POME) (Borja and Banks, 1994c). UASB has a relatively simple design where sludge from organic matter degradation and biomass settles in the reactor. Organic matter from wastewater that comes in contact with sludge will be digested by the biomass granules.

2.2.1.5 Anaerobic filters

The anaerobic filter (AF) has been widely applied in the beverage, food-processing, pharmaceutical and chemical industries due to its high capability of biosolids retention.

Anaerobic filter were favoured for wastewater treatment as a results of the following:

- High substrate removal efficiency
- It requires a smaller reactor volume which operates on a shorter hydraulic retention times (HRT), (Borja and Bank, 1994b),
- The ability to maintain high concentrations of biomass in contact with the wastewater without affecting treatment efficiency(Reyes *et al*., 1999; Wang and Bank, 2007),
- Tolerance to shock loadings (Reyes *et al*., 1999; Van Der Merwe and Britz, 1993).

Also, construction and operation of anaerobic filter is less expensive and small amounts of suspended solids in the effluent eliminate the need for solid separation or recycle (Russo *et al*. 1985). Anaerobic filters have been applied to treat various types of wastewater including soybean processing wastewater (Yu *et al*., 2002a); wine vinases (Nebot *et al*., 1995; Perez *et al*., 1998); land fill leachate (Wang and Bank., 2007), municipal wastewater (Bodkhe, 2008), brewery wastewater (Leal *et al*., 1998), slaughterhouse wastewater (Ruiz *et al*., 1997), drug wastewater (Gangagni *et al*., 2005), and beet sugar water (Farhadian *et al*., 2007).

2.2.1.6 Anaerobic film reactors / fluidized bed

The anaerobic fluidized bed (AFB) reactor is a type of reactor device that can be used to carry out a variety of multiphase chemical reactions. It comprises small media, such as sand or granular activated carbon, to which bacteria attach. Good mass transfer resulting from the high flow rate around the particles, less clogging and short-circuiting due to the large pore spaces, formed through bed expansion and high specific surface area of the carriers (Borja *et al*., 2001) due to their small size make fluidized bed reactors highly efficient. However, the lapses include difficulty in developing strongly attached biofilm containing the correct blend of methanogens, detachment risks of microorganisms, negative effects of the dilution near the inlet as a result of high recycle rate and high energy costs due to the high recycle rate are the main drawbacks of this system (Ersahin *et al*., 2011).

Investigations have been carried out on the application of fluidized bed to treat cutting-oil wastewater (Perez *et al*., 2007); real textile wastewater (Sen and Demirer, 2003); slaughterhouse wastewater (Toldra *et al*., 1987); wine and distillery wastewater (Garcia *et al*. 1998),(Sowmeyan and Swaminathan, 2008); ice-cream wastewater (Borja and Bank, 1995a), (Hawkes *et al*., 1995); pharmaceutical effluent (Saravanane *et al*., 2001), and POME (Borja and Bank., 1995b)

A lab-scale AFB reactor using cultivated polyvinyl alcohol gel beads with a diameter of 2–$^{-}$ mm, to treat corn steep liquor was investigated by Zhang *et al*. (2009). The effective volume of the reactor was 3.9 L. Influent COD concentration varied within 2100-12900 mg/L. COD removal efficiencies of 96% and 91% were achieved at Organic Loading Rate (OLRs) of 27.5 and 25 kg COD/m^3.day with HRTs of 10 h and 6 h, respectively. 610 g/L of biomass concentration was achieved by the biomass attachment of 1.02 g volatile suspended solid/g PVA-gel beads.

2.2.2 Chemical and Physical Methods

Chemical and Physical methods include ozonisation, adsorption, ion exchange, membrane filtration, chemical oxidation etc (Arutchelvan *et al*., 2006; Aksu and Gonen, 2006; Meghraj *et al*., 2003; Das and Mishra, 2010). These process are high energy consuming, non economic and release effluents and waste waters which require further treatment. Also, complete removal of the pollutants is not possible by the use of physical and chemical processes

(Camargo *et al*., 2003; Shen and Wang, 1994; Wang and Chirwa, 1998).

2.2.2.1 Ozonisation

Chemical oxidation with ozone can be used to treat organic pollutants or act as disinfectant agents. Ozone has been applied to the treatment of waters primarily due to its strong disinfection and sterilisation properties (Araña *et al*., 2002). Ozone is a powerful oxidant that can oxidize a great number of organic and inorganic materials. Ozone based technologies research is also focused on the catalytic ozonation where the presence of catalyst significantly improved the oxidation rate of organic compounds compared to non catalytic ozonisation. The ozonisation processes are possibly one of the most effective methods for treatment of wastewater containing organic products such as effluents from chemical and agrochemical industries, textile industry, paints, etc. (Guendy, 2007). The use of high oxidation potential like ozonisation has recently received much attention in wastewater treatment studies. A Ozoniser in which the oxygen molecules in the gas were dissociated to form ozone was used in many cases (Matheswaran *et al*., 2007).The disadvantages associated with the process are high operating cost and cost of equipment. The cost of the equipment is very high and also it requires high voltage and electricity for its operation (Larsen *et al*., 2004; Gharbani *et al*., 2010). The main mode of action in the ozonation process is the formation of OH- radicals due to ozone decay in the water, but there are also ozone molecules present for chemical attack. This increases the oxidation capacity (Ternes *et al*. 2003). However, the characteristics of the wastewater such as pH, temperature and concentration of organic pollutant play an important role in organic degradation (Yogeswary *et al*., 2005). Similarly, Wang *et al*. (2008), have studied the treatment of industrial effluents by with varied ozone concentrations. Initial pH and dosages of catalyst were also varied. The remaining organic matter was removed by BAF (Biological aerated filter), and the effect of hydraulic retention time (HRT) of BAF was also considered. Their result showed that under optimum pH and dose of H_2O_2 about 30% COD could be removed by ozonisation alone.

2.2.2.2 Ion exchange

Ion exchange involves the removal of an ion from an aqueous solution by replacing with another ionic species. Ion exchange can be used for the removal of undesirable anions and cations from a wastewater. Cations are usually exchanged for hydrogen or sodium ions, and anions for hydroxyl ions. Ion exchange resins consist of an organic or inorganic network structure with attached functional groups. There are natural and synthetic materials available which are specially designed to enable ion exchange operations at high levels. Most ion exchange resins used in wastewater treatment are synthetic resins made by the polymerisation of organic compounds into a porous three-dimensional structure. Synthetic and industrially produced ion exchange resins are mainly made up of polystyrene and polyacrylate which are in the form of small and porous beads. Also there are some naturally occurring minerals which have ion exchange properties. The most common one is aluminium silicate minerals which are also called zeolites (Raghu *et al*., 2007). There are different zeolites made up of various ionic materials which have affinity towards some particular metals. The main characteristics of the ionic resins are material properties such as adsorption capacity, porosity, density etc (Zorpas *et al*., 2010).Ion exchange resins are called *cationic* if they exchange positive ions and *anionic* if they exchange negative ions. Cation exchange resins are comprised of *acidic* functional groups, such as sulphonic groups, whereas anion exchange resins have *basic* functional groups, such as amine. The strength of the acidic or basic character depends upon the degree of ionisation of the functional groups, similar to the situation with soluble acids or bases. Thus, a resin having sulphonic acid groups would act as a strong acid cation exchange resin. The main disadvantages associated with ion exchange methods are the high cost of the ion exchange resins and the selective nature of the resins in the removal of selective contaminant only. Furthermore, complete removal of the contaminant is not possible. Besides, ion exchange can be used for limited cycles only because passing concentrated metal solution the matrix gets easily owned out by organics and other solids in the wastewater after several use. Moreover ion exchange is sensitive to pH of the solution (Liotta *et al*., 2009; Sapari *et al*., 1996).

A comparative study of alginate beads and an ion-exchange resin for the removal of heavy metals from a metal plating effluent was studied (Silva *et al*., 2008). It was observed that alginate beads removed lower amounts of heavy metals than the resin, but exhibited faster uptake kinetics. The comparison of dry protonated alginate beads with the resin supports the potential of the biosorbent for the treatment of industrial effluents. Howard *et al*. (2009) used ion exchange technology in the purification of gold mine water for discharge or re-use as industrial or potable water. The technology produced water quality that met the limits for discharge into water bodies. Gayathri and Senthi- Kumar (2010) also conducted the recovery and reuse of hexavalent chromium from aqueous solutions by a hybrid technique of electrodialysis and ion exchange. The different modes of operation, such as batch recirculation process, batch recirculation process with continuous dipping and continuous process, were carried out to remove and recover the chromium from the effluent. The reductions of chromium were found to be 98.69%, 99.18% and 100%, respectively.

2.2.2.3 Adsorption

Adsorption is a widely used method for the treatment of industrial wastewater containing colour, odour, heavy metals and other inorganic and organic impurities, (Lai and Lin, 2003; Ganji *et al.*, 2005; Al Rekabi *et al.*, 2007; Georg Steinhauser 2008; Patel and Vashi, 2010). Adsorbent materials are basically derived from low-cost agricultural wastes,activated carbon prepared from various raw materials such as sawdust, groundnut husk, nut shells, coconut shells etc (Olayinka and Osinowo, 1999; Brown *et al.* 2000; Fischer *et al.*, 2002; Zawani *et al.*, 2009).These adsorbents are used for the effective removal and recovery of organic and metal pollutants from wastewater streams (Basso *et al.*, 2002 and Park *et al.*, 2006). It is a complex process affected by several factors. Mechanisms involved in the adsorption process involves the particle size, surface area and porosity of adsorbent etc (Gardea-Torresdey *et al.*, 2004).This method suffers from low adsorption capacity and in some cases complete removal is not possible and the cost of adsorbent is high. After use the disposal of adsorbents create problems.

2.2.2.4 Membrane filtration

Membrane filtration technique has received a significant attention for the wastewater treatment. It considers the application of hydraulic pressure to bring about the desired separation through the semi permeable membrane (Chen *et al.*, 2005). Membranes are of different pore size and it is necessary to select membranes of appropriate pore size for specific purpose so that effluent and wastewater could be purified and permeable membrane could be recycled a number of times. There are three types of membrane filtration. These are ultra-filtration, nanofiltration and reverse osmosis (Chauhan and Rekha, 2004; Al-Rekabi *et al.*, 2007). Various other types of membranes such as inorganic, polymeric, and liquid membranes can be used for this process. The main problem associated with this process is incomplete removal of contaminants, high energy requirement, high cost of the membrane and longevity of the membrane. After long term use the membranes get clogged with the contaminants present in the waste water and are damaged due to extra pressure on it.

2.2.2.5 Chemical oxidation

In this process the waste materials from the industrial waste water are removed by the help of chemical oxidation using various chemicals mainly hydrogen peroxide (Dias-Machado *et al*., 2006; Ksibi, 2006). There are many disadvantages associated with this process like the high cost of the chemicals, emission of various harmful by products, hazardous constituents like secondary effluent problem along with the production of harmful gases

2.2.2.6 Chlorination

Chlorine, a strong oxidizing chemical, is used to kill bacteria and to slow down the rate of decomposition of the wastewater. Bacterial kill is achieved when vital biological processes are affected by the chlorine. Another strong oxidizing agent that has also been used as an oxidizing disinfectant is ozone. Chlorination has been shown to be effective for the removal of pharmaceuticals including 17α- ethinylestradiol and 17 β-estradiol (Alum *et al*., 2004) and sulfonamides (Qiang *et al*., 2006). Chlorine dioxide is also effective for the removal of sulfamethoxazole, roxithromycin, 17α-ethinylestradiol and diclofenac (Khetan and Collins, 2007).

2.2.2.7 Neutralization

A chemical process commonly used in many industrial wastewater treatment operations is neutralization. Neutralization consists of the addition of acid or base to adjust pH levels back to neutrality. Since lime is a base it is sometimes used in the neutralization of acid wastes.

2.2.2.8 Coagulation

Coagulants used for treatment of both water and wastewater treatment are predominantly inorganic salts of ferric iron or aluminium. Aluminium salts, including aluminium sulphate and aluminium chloride, in addition to pre-hydrolysed metal-ion reagents such as poly-aluminium sulphate and poly-aluminium chloride (PAC), are the coagulants most widely used for water treatment (Bratby, 1980; ACWA, 2000). A possible alternative is to use iron-based coagulants, such as ferric chloride, ferric sulphate, or poly-ferric sulphate instead of the aluminium salts (Tenny and Derka, 1992; Jiang *et al*., 1996; Jiang and Graham, 1998). However, the coagulants composed by a mixture of both aluminium and iron salts can also be applied in water treatment. A study conducted by Jiang and Graham (2003) demonstrated that a poly-alumino-iron sulphate coagulant (PAFS) achieved, in water treatment tests, either a greater or similar removal in terms of percentage of colour and dissolved organic carbon in comparison with other conventional coagulants. The authors demonstrated that the PAFS allowed lower residual metal-ion concentrations in the drinking water when compared to poly-ferric sulphate, ferric sulphate, and aluminium sulphate

2.3 THE LAGOS ENVIRONMENT

Lagos is highly populated and there are quite a number of industries distributed across the city, a development that has put the city under serious pressure in terms of environmental safety. Consequently, the city and its environs have witnessed environmental degradation leading to decreased biodiversity and extinction of many sensitive organisms (Odjegba and Bamgbose, 2012). Most of the industries in Lagos State do not control their wastewater effluents by processing, waste recycling or end-of-pipe treatment. Thus, effluents with some levels of toxic substances are being discharged into the environment untreated

The discharge of partially treated or untreated industrial effluents into water bodies is a common phenomenon in Lagos metropolis. Table 2.1 lists the sources/types of industrial wastes in the Lagos area which are discharged either directly or indirectly into the lagoon systems, and their potential threats to aquaculture. These wastes and the resultant pollutants could bring about reduction in dissolved oxygen levels, eutrophication and increase in temperature. They could also cause increased organic load, increased turbidity as well as damage to nurseries and spawning grounds. Due to inability to sort waste at source, household and industrial waste, including toxic ones, are often handled together, leading to soil and ground water pollution (UNESCO, 2000).

The indiscriminate discharge of chemical toxins especially Pb, Cd, Cr, Co, etc. into the environment ensure their transfer into plants, animals and man. The high concentration of heavy metals in irrigation waters could results in death of crops, interfere with uptake of other essential nutrients or form objectionable deposits on fruits. This may render the edible portions of plants toxic to humans and grazing animals (UNESCO, 2000). A study on fundamentals and trends of water services in Nigeria urban settlement Sangodoyin (1990) showed concern in an increase in the level of pollutants in surface and ground water which services as a source of domestic water and sometimes drinking water for rural and urban dwellers in Nigeria. Sangodoyin (1995) studied characteristics and control of industrial effluents generated pollution and showed that increase industrial activities have led to

Table 2.1: Pollutant characteristics of wastes from some Lagos industries.

Source	**Pollutants**	**Threat to Aquaculture**	**References**
Brewing: e.g.Dumex Industry (Nig) Ltd., Vitamalt Plc	Organic pollutant, alcoholic brewer waste, biodegradables, Zn, Pb, Ca, Mg, sulphate	Low dissolved oxygen, eutro-phication, pollutants get clogged in the gills of fish	Ajao (1990)
Pulp & Paper: e.g. WTN Plc	Sulphate, free chloride, caustic soda, chlorine dioxide and hypochlorite	Moderately toxic and can easily be bioaccumulated. Elevated levels of some metals in sediments and biota.	Ajao (1996)
Soap Manufacturing: e.g. Lever Brothers Plc, Lorry Parks/Mechanic	Detergent, caustic soda from washing and cooling water, sulphurated detergent, oil, grease, engine oil, petrol.	Prevent penetration of light, low dissolved oxygen in water, prolific growth of blue-green algae and bacteria, eutrophication.	FEPA (1992)
Plastics Industry: Lotus Plastic	Hot polymer by-products, calcium, tin and lead.	Increases the temperature; bioaccumulation of metals often result.	FEPA (1992)
Foods Industry: e.g. International Quality Food (Nig) Ltd., Unilever Brothers Plc	Organic pollutants and biodegradables. Elevated water temperature	Eutrophication, pollutants get clogged in the gills of the fish; low dissolved oxygen.	FEPA (1992)
Chemical Industry: Henly Industries (Nig) Ltd, Drury (Nig) Ltd,, Reckitts and Beckiser, Colodense (Nig) Ltd.	Acid, alkali, caustic soda, insecticides, detergent, free chloride, rodenticides, polymer and nylon.	Low dissolved oxygen, reduced temperature, highly toxic to fish, obstruct balance of food chain and bioaccumulation.	FEPA (1992)
Pharmaceuticals: Pharma Deko, Evans (Nig) Ltd., Glaxo Smithkline Plc	Free chloride, detergent, pesticides, organic pollutants and trace metals, alkali.	Bioaccumulation, toxic to fish, fish kill and low dissolved oxygen.	FEPA (1992)
Metal Finishing: e.g. John Edge Company (Nig), Beta Glass	Acids, alkali, fluoride, inorganic salt, cyanide, phosphate, toxic metals - Zn, Pb; S, sulphur	Highly toxic, fish kill, low dissolved oxygen, high BOD.	FEPA (1992)

Source	Pollutants	Threat to Aquaculture	References
	compounds		
Industries Generating Hydrocarbon Wastes:	Oil and grease.	Undesirable thick black flames of oil in sheltered waters, reduction in light penetration, loss of plankton, reduced dissolved oxygen, anoxic condition in bottom sediments, risk to aquatic organisms and fish-eating birds.	Ajao (1990)

pollution of our major rivers and streams in Nigeria.

Effluents from industries have been known to contaminate water, soil and air with associated heavy disease burden and eventual shorter life expectancy in developing countries (WHO, 2003). The presence of poisonous chemicals in industrial effluents may pose health threats to humans and animals. Studies relating to the physicochemical characteristics of different types of industries in Lagos are few. Textile industry wastewaters are one of the principal sources of pollution in the world (Olayinka and Alo (2004). In particular, the release of coloured effluents into the environment is undesirable, not only due to their colour, but also because many synthetic dyes and their breakdown products are toxic and/or mutagenic (Saratale *et al.*, 2009; Ben Younes *et al.*, 2011).

The physicochemical pollutant indicators from textiles industries (Adebayo *et al.*, 2007; Awomeso *et al.*, 2010) were studied in Lagos, and it was noted that the levels of pH, alkalinity, biological oxygen demand, chemical oxygen demand and dissolved oxygen were higher than the guideline limits of NESREA. The effect of textile effluent on groundwater was studied by Olayinka and Alo (2004). The study showed that the effluents had high values of BOD_5 (100–390 mg/l) and COD (204–2000 mg/l) and were highly coloured. These values were higher than the effluent limits stipulated by the Federal Ministry of Environment for textile industries.

2.4 USE OF MULTIVARIATE STATISTICAL TECHNIQUES TO GENERATE LINEAR REGRESSION MODEL FOR ENVIRONMENTAL STUDIES

The application of different multivariate statistical techniques, such as principal component analysis (PCA), factor analysis (FA) and discriminant analysis (DA), helps in the interpretation of complex data matrices to better understand the water quality and ecological status of the studied systems. It allows the identification of possible factors/sources that influence water systems and offers a valuable tool for reliable management of water resources as well as rapid solution to pollution problems (Helena *et al*. 2000; Lee *et al*. 2001; Adams *et al*. 2001; Wunderlin *et al*. 2001; Reghunath *et al*. 2002; Simeonova *et al*. 2003; Simeonov and Tisitouridou, 2004; Papatheodorou *et al*. 2007).Multivariate statistical techniques has been applied to characterise and evaluate surface and freshwater quality, and it is useful in verifying temporal and spatial variations caused by natural and anthropogenic factors linked to seasonality. For example, Zou and Yu (1996) have used a general dynamic factor model to reduce the high dimensionality of the original matrix variables in order to detect trends in time series. Meng and Maynard (2001) used cluster and factor analysis to identify geochemical regions within a watershed in Brazil. Silva and Williams, (2001) combined multivariate statistical analyses with GIS (Geographical Information System) analysis to determine if a correlation existed between water quality and landscape characteristics in a watershed in southern Ontario (Canada). Singh *et al*. (2004) and Singh *et al*. (2005) used multivariate statistical techniques to evaluate spatial and temporal variations in water quality of the Gomti River (India). Similarly, Shrestha and Kazama (2007) also used multivariate statistical techniques to assess the surface water quality of the Fuji River Basin in Japan. These techniques, especially PCA, have also been used to evaluate the water quality monitoring stations (Ouyang, 2005). Furthermore, long term hydrochemical data of shallow water bodies have been evaluated using factor analysis and discriminant analysis (Medina-Gomez and Herrera-Silverira, 2003; Solidoro *et al.*, 2004). Statistical models are developed for estimation of concentration of different water quality constituents using routinely-monitored water quality parameters. The best subset modeling procedure enables comparison between full models (containing all the independent variables). Best subset procedure based on R^2 and F values can be used in model dissemination (Sharma and Jain, 2005). Correlation and regression analysis have been described for the study of land use and non point source impacts on water quality (Rajendra *et al.*, 2009). SPSS software can be used to generate Linear Regression Model using the data obtained from the effluent quality analysis.

2.4.1 Effluent Quality Model

Models are a set of mathematical expressions (partial or ordinary differential or algebraic equations) describing the physical, biological, chemical, and economic processes which take place in a system (e.g. waste water). The challenge of using mathematical modeling, as a support tool to evaluate remediation options in developing countries is well documented (Ongley and Booty, 1999). However, modeling is expensive, requires substantial investments in reliable data, development of scientific capacity and a relatively sophisticated management culture that are often not found in developing countries. Regression models, linear time series models, non linear time series analysis and artificial neural networks have been used for variety of purposes, such as forecasting, rainfall runoff modeling, estimation of missing hydrologic data, and modeling of water quality parameters in streams (Ongley and Booty, 1999).

A modeling approach with at least seven specific characteristics is needed. These characteristics are:

- The watershed or any hydrologic system, are to be described and simulated in a simple fashion.
- The model should start simple, relying on the available data.
- The model should be adequately dynamic to cope with the nature of hydrologic systems.
- The model should have the ability to simulate both linear and nonlinear processes.
- The model needs to provide a way to represent the feedback mechanism in order to handle counter intuitive processes.
- The model should have the ability to model human intervention and any shocks that might be encountered in the system and;
- The model should have the ability to test different policy or management scenarios for better decision making.

2.4.2 Model Classification

Water quality models are usually classified according to model complexity, type of receiving water and the water quality parameters (dissolved oxygen, nutrients, etc) that the model can predict. The more complex the model is the more difficult and expensive will be its application to a given situation (Thomann and John, 1987). Model complexity is a function of four factors:

- The number and type of water quality indicators: in general, the more indicators that are included, the more complex, the model will be. Some indicators are more complicated to predict than others.
- The level of spatial detail: as the number of pollution sources and water quality monitoring increase, so do the data required and the size of the model.
- The level of temporal detail: it is much easier to predict long-term static averages than short term. Dynamic changes in water quality parameters estimates are usually simpler than stochastic predictions of the probability distributions of these parameters.
- The complexity of the water body under analysis: small lakes that “mix” completely are less complex than moderate-size Rivers which are less complex than large rivers, estuaries, and coastal zones.

The level of details required can vary tremendously across different management applications. Models can cover only a limited number of pollutants. In selecting parameters for the model, care should be taken to choose pollutants that are a concern in them and are also representative of the broader set of substances which cannot all be modeled in detail.

Simulation models are used to predict a system response to a given design configuration with great accuracy and detail and to identify the probable costs, benefits and impacts of a project. That is, the simulation model predicts the outcome of a single, specified set of design or policy variables. However, the space of possible design and policy variable values is in general, infinite. Separate simulation model runs are required for each design or policy alternative considered. In many situations the number of alternative designs is sufficiently large to preclude simulating each alternative designs and some other method is normally used to narrow the field of search.

Optimization models provide a means of reducing the number of alternatives which need to be simulated in detail, i.e. screening them. Those models search the space of possible design variable values and identity an optimal design and/or operating policy for a given system design objective and sets of constraints. These models include relationships which describe the state variables and costs or benefits or each alternative as a function of the decision variables.

The assessment of long-term water quality changes is also a challenging problem. During the last decades, there has been an increasing demand for monitoring water quality of many rivers by regular measurements of various water quality variables. The result has been the gradual accumulation of reliable long-term water quality records and the examination of these data for long-term trends (Hirsch *et al*., 1991). Computer systems now offer the possibility of handling and manipulating very large databases in ways which were not previously a practical option. Littlewood *et al*. (1998) have used such databases for estimation of UK river mass loads of pollutants. Miller and Hirst (1998) used the hydrochemical databases from an upland catchment in Scotland for a period of five years to assess the annual variation in amounts and concentration of solutes and to examine the variation in stream water quality due to changes in flow, season and long time trend. Ferrier *et al*. (2001) analyzed in details databases for Scotland and identified temporal changes in water quality over the last 20 years.

2.5 APPLICATION OF MULTIPLE LINEAR REGRESSION MODEL TO WATER QUALITY PREDICTION

Multiple regression analysis is a statistical tool for understanding the relationship between two or more variables. Multiple regression examines the relation between a single dependent variable and a set of independent variables to best represent the relation in the population. The technique is used for both predictive and explanatory purposes within experimental or non experimental designs (Tinsley and Brown 2000). When there are an arbitrary number of explanatory variables, the linear regression model takes the following form:

$$Y = \beta_0 + \beta_1.X_1 + \beta_2.X_2 + \dots\dots\dots\dots + \beta_m.X_m + e_{ij}$$

where Y represents the dependent variable and $X_1 \dots X_u$ represent the different independent variables, $\beta_0, \dots \dots, \beta_m$ represent the regression coefficient and e represents the random error (Freund and Wilson 1998). The error term e represents the collective unobservable influence of any omitted variables. In a linear regression each of the terms being added involves unknown parameters, which are estimated by “fitting” the equation to the data using least-squares.

It has been used to investigate relationships between water quality parameters (physicochemical and biological) and landscape characteristics (Sliva and Williams 2001; Wang 2001; Singh *et al*. 2005; Amiri and Nakane 2009) and to investigate between water quality and pathogen indicators (Mallin *et al*. 2000; Crowther *et al*. 2001). MLR models typically make use of easily measured environmental and water-quality variables to estimate pollutant concentration.

CHAPTER THREE

MATERIALS AND METHODS

3.1 DESIGN OF STUDY

The experimental procedures were designed in line with the broad aims and objectives of the study as indicated in section 1.3., i.e. to determine the characteristics of the effluents of some industries located in three industrial estates in Lagos, and determine suitable chemical treatment options. The design components included the following:

(a) Selection of Industrial Estates for the Study: Three estates were selected for this study. They were sufficiently representative of the industrial estates in the Lagos area with respect to age, types of industries within the estates, and accessibility to the effluent channels. In each estate, only some of the industries were investigated. The list of estates and the industries investigated are given below:

(i) **Ikeja Industrial Estate**:

- a pharmaceutical industry - May & Baker (Nigeria) Plc;
- a paints industry - Berger Paints (Nigeria) Plc;
- a textile industry - Woolen and Synthetic Textile Manufacturing Limited;
- two basic metal industries – Galvanizing Industries Limited, and Hoesch Pipe Mills Ltd.
- a central effluent treatment plant for the estate, owned and operated by WEMABOD.

(ii) **Isolo Industrial Estate**:

- two pharmaceutical industries – Johnson Wax Nig. Ltd, and Afrab Chem Ltd.
- a food and beverages industry - Viju Industries Ltd. (*N.B: this industry is now located in Ikeja, but was located in Isolo at the time of the study*).

(iii) **Ilupeju Industrial Estate**:

- a conglomerate (varied products) industry – PZ Industries Nig. Plc.
- a nearby canal receiving industrial wastewater discharge.

(b) Study of Effluent Characteristics:

Location of Sampling Points: For a particular factory/industry, effluents samples were collected along the discharge channel, at an accessible point closest to the factory. Two points at about 100 m apart were sampled along the canal, while the underground tunnel at the treatment plant was also sampled.

Frequency/Duration of Sampling: Sampling was carried out bimonthly at each sampling location, and lasted a period of 20 months (November 2006 to May 2008), covering (two wet and two dry seasons).

Parameters Determined:

- Physicochemistry - pH, conductivity, total dissolved solid, alkalinity, total hardness, calcium, magnesium, chloride, sulphate, phosphate and nitrate.
- Heavy metals - Pb, Cd, Zn, Cu, Cr and Ni
- Gross Organic Pollutants - dissolved oxygen, biochemical oxygen demand, and chemical oxygen demand.

(c) Study of Sediments Obtained from Effluent Channels: Sediments are good indicators of depositions from fluid/aquatic systems, as sediment quality reflect long-term characteristics of the fluid medium above the sediments. Thus, even for an effluent channel, the drainage sediment is a good sink for indirectly monitoring pollutant in the liquid effluents.

Location of Sampling Points: Sediments were obtained at the locations where effluents were sampled. *However, it was not possible to obtain sediments at all effluent sampling points, as no sedimentation occurred at such points*.

Frequency/Duration of Sampling: Sediment sampling was of the same frequency and duration as the effluent sampling.

Parameters Determined:

- Physicochemistry - pH, % organic carbon and mechanical property (particle size)
- Heavy metals- Pb, Cd, Zn, Cu, Cr and Ni

(d) Study of Topsoil Quality Around Some Effluent Channels: Quality of topsoil beside the effluent channels was studied at two of the estates because it was observed that the sediments were often scooped out of the channels and deposited on adjoining grounds. The topsoil quality was thus determined to examine the relationship with the qualities of the sediments and effluents.

Location of Sampling Points: Samples of topsoil collected at various points directly beside (not more than one metre) the drainage channel. At Isolo estate, six sampling points were utilized around the channel, while at Ikeja estate, four locations were utilised.

Frequency/Duration of Sampling: Frequency and duration were same as for effluents and sediments.

Parameters Determined: Same as for sediments.

(e) Treatment of Textile Effluent: From the results obtained from the effluent characterization study, it was noted that the most highly organically polluted effluents were those obtained from the textile and pharmaceutical industries with extreme values of BOD and COD. The textile industry effluents were then selected for testing the efficiencies of a variety of treatment methods for the reduction of the organic load. The following treatment options were investigated:

- Treatment with Fenton's reagents ($FeCl_2.4H_2O$ and H_2O_2 ; $FeSO_4.7H_2O$ and H_2O_2; $FeCl_2$ $.4H_2O$ + $FeSO_4.7H_2O$ and H_2O_2.
- Treatment with a variety of inorganic coagulant chemicals – $FeCl_2.4H_2O$, $FeSO_4.7H_2O$, $FeCl_3$, alum
- Treatment with activated charcoal
- Simple exposure of effluent to the dark and under sunlight, with no addition of chemicals.

Parameters for Monitoring the Effectiveness of Treatment: pH, total dissolved solid, total suspended solids and chemical oxygen demand.

(f) *Model Estimate of Organic Pollutant Loading and Potential for Eutrophication*: The results obtained from the physicochemical characterisation were utilised for developing a model for predicting the phosphate and COD levels in effluents based on the observed levels of other parameters. Such COD levels reflect the potential for organic loading, while the phosphate levels reflect the potential for eutrophication. Both modeled parameters are significant for predicting the impact of the effluents on the receiving streams and Lagoon.

The modeling was based on application of stepwise multiple linear regressions to obtain a model equation for estimating:

- organic pollutant load (as chemical oxygen demand), and
- potential for eutrophication (as phosphate concentrations)

3.2 DESCRIPTION OF STUDY LOCATIONS

The various industrial estates studied and the effluents sampling points from the industries are shown in Figure 3.1, Figure 3.2 and Figure 3.3. Table 3.1 gives the site codes, while Table 3.2 describes the features of the sampling locations. Appendix 1 shows the GPS derived geographical locations of the sampling points.

3.3 SAMPLING

3.3.1 Preparation of Sample/Sampling Containers

polyethene containers for effluents samples were washed with detergent and rinsed with water. The containers were soaked in 2 M nitric acid overnight and then washed with distilled water prior to sampling. Winkler bottles for dissolved oxygen were also cleaned as described for the polythene containers. The hand trowel used for collecting sediments/soil samples was washed with detergent and rinsed with distilled water prior to sampling. Clean hand trowel was used to collect the sediments/soil samples

3.3.2 Collection of Effluent

At each sampling point, a composite effluent sample was collected by dipping a clean polythene plastic cup into effluent at the discharge point and pouring into the storage clean polythene plastic bottle for physicochemical parameters. Samples for heavy metal were collected into other polythene plastic bottles and preserved by addition of 2 mL of conc. nitric acid to 1L of effluent at the site.

By this method a total of 60 effluent samples were obtained from various industries in Ikeja Industrial Estate during the study period. The corresponding numbers for Isolo and Ilupeju estates were 55 and 47.

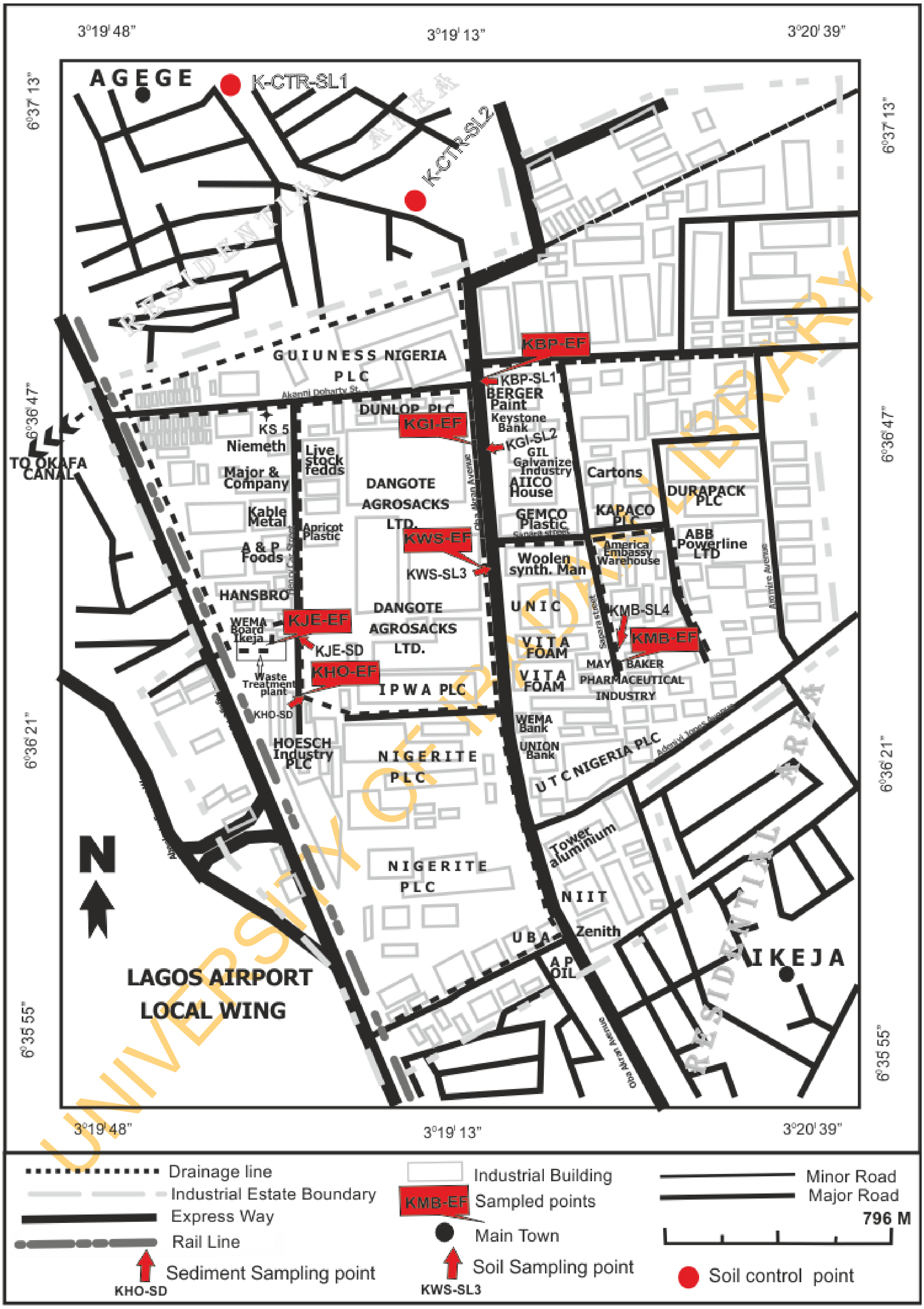

Figure 3.1: Map of Ikeja Industrial Estate showing sample locations.

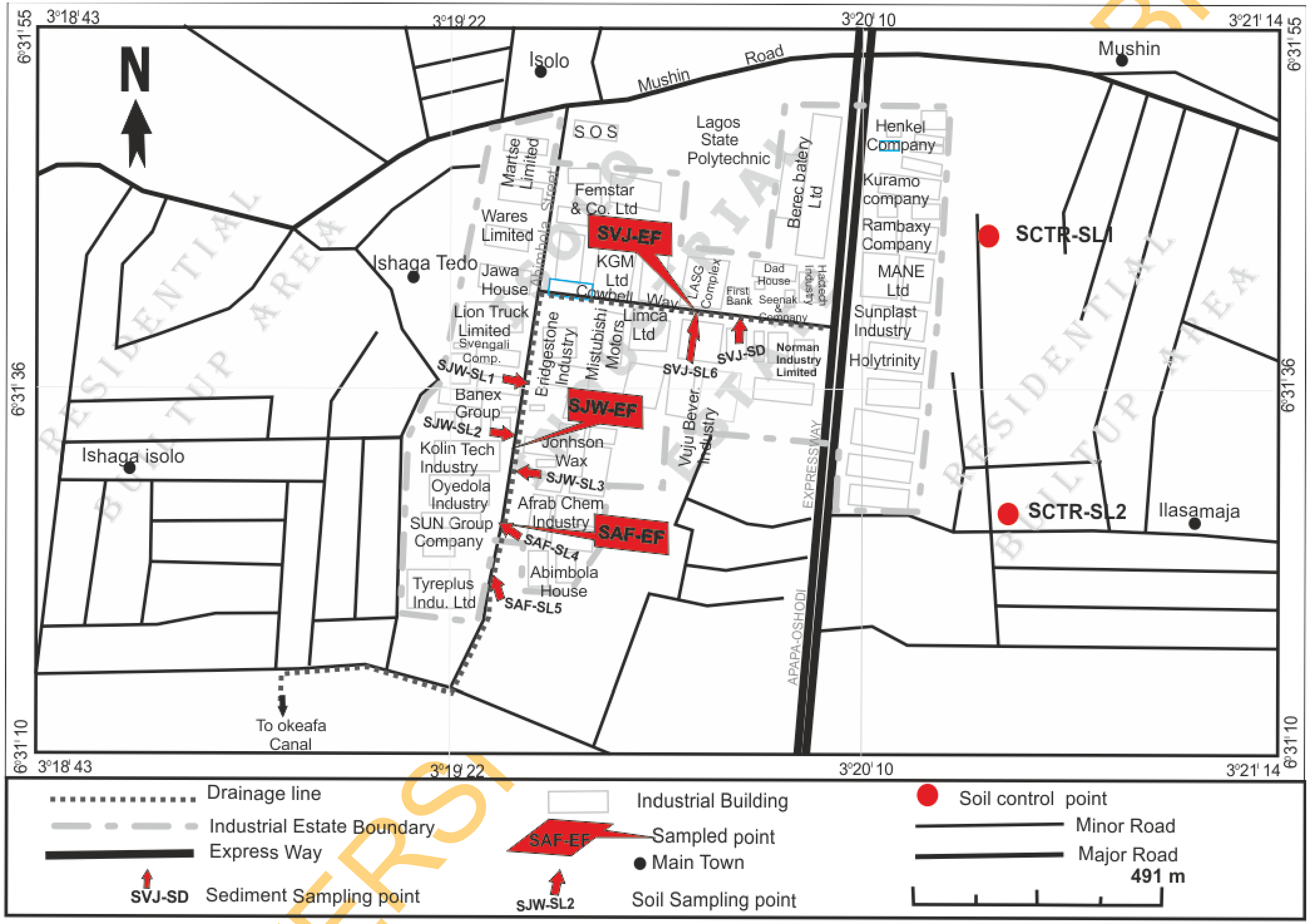

Figure ¯.2 :Map of Isolo Industrial Estate showing sample locations.

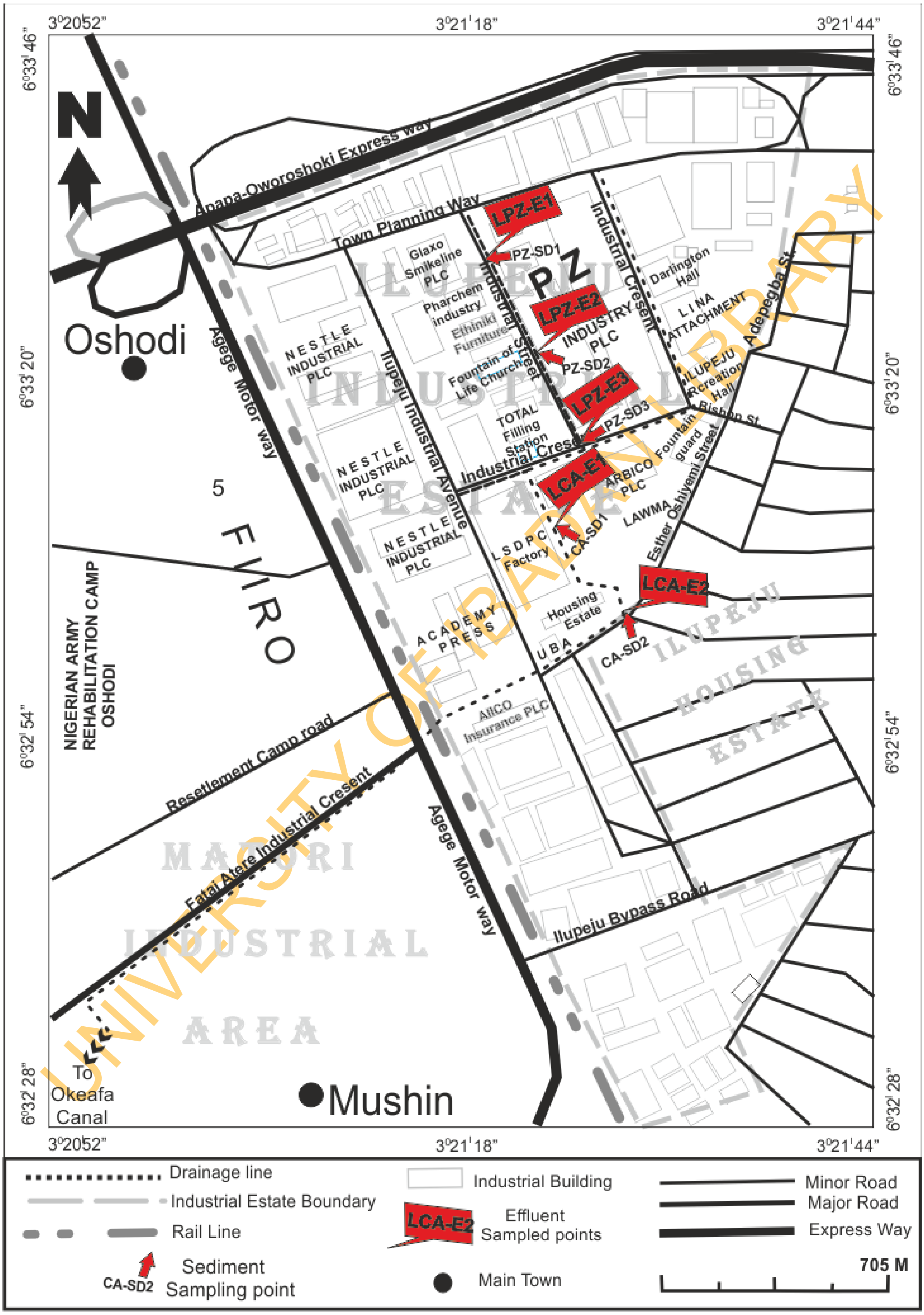

Figure 3.3: Map of Ilupeju Industrial Estate showing sample locations.

Table 3.1: Industries sampled from various industrial estates

Name of Industrial Estate	**Industry Sampled**	**Classification**	**Site Code**
Ikeja Industrial Estate	Hoesch Pipe Mills Ltd.	Basic metal	KHO
Ikeja Industrial Estate	Berger Paints (Nigeria) Plc	Paint industry	KBP
Ikeja Industrial Estate	Galvanizing Industries Limited	Basic metal	KGI
Ikeja Industrial Estate	Woolen and Synthetic Textile Manufacturing Limited	Textile industry	KWS
Ikeja Industrial Estate	May & Baker (Nigeria) Plc	Pharmaceutical	KMB
Ikeja Industrial Estate	Central Treatment Plant	-	KJE
Isolo Industrial Estate	Johnson Wax Nig. Ltd	Pharmaceutical	SJW
Isolo Industrial Estate	Afrab Chem	Pharmaceutical	SAF
Isolo Industrial Estate	Viju industries	Food &beverages	SVJ
Ilupeju Industrial Estate	PZ Industries Nig. Plc	Conglomerate*	LPZ
Ilupeju Industrial Estate	Canal **	-	LCA

* varied product (pharmaceuticals, cosmetics and house hold appliances) types industry.

** Canal receives effluents discharged from several industries

Table 3.2: Description of sample locations and code.

Sample Code	Type of Sample	Location	Location Features
KHO-EF	Effluent	Ikeja Industrial Estate	Open drainage from metal industry, close to abandoned treatment plant; shallow - about 1.5m depth; varied colours and offensive odour (Appendix 2)
KBP- EF	Effluent	Ikeja Industrial Estate	Open drainage from paint company; shallow with about 1.5m depth; varied colours and offensive odour
KGI- EF	Effluent	Ikeja Industrial Estate	Open drainage from galvanizing industry; shallow with about 1.5m depth; varied colours and offensive odour
KWS- EF	Effluent	Ikeja Industrial Estate	Open drainage from textile company; shallow with about 1.5m depth; varied colours and offensive odour
KMB- EF	Effluent	Ikeja Industrial Estate	Open drainage from pharmaceutical company; shallow with about 1.5m depth; varied colours and offensive odour (Appendix 3)
KJE- EF	Effluent	Ikeja Industrial Estate	Open sewer (abandoned treatment plant) with vegetation; receives all the effluents on the estate; have a depth of about 3.0m, coloured with offensive odour (Appendix 4)
SJW- EF	Effluent	Isolo Industrial Estate	Open drainage from pharmaceutical company; has a depth of about 1.0m; varied colours and offensive odour (Appendix 5)
SAF- EF	Effluent	Isolo Industrial Estate	Open drainage from pharmaceutical company; has a depth of about 2.0m; varied colours and offensive odour (Appendix 6)
SVJ- EF	Effluent	Isolo Industrial Estate	Open drainage from food and beverage industry; has a depth of about 1.0m; varied colours and offensive odour

Table 3.2: contds.

Sample Code	Type of Sample	Location	Location Features
LPZ- EF1	Effluent	Ilupeju Industrial Estate	Open drainage from a conglomerate company; has a depth of about 1.0m; varied colours and offensive odour
LPZ- EF2	Effluent	Ilupeju Industrial Estate	Open drainage from a conglomerate company ; has a depth of about 1.0m ; varied colours and offensive odour
LPZ- EF3	Effluent	Ilupeju Industrial Estate	Collective effluent joint from a conglomerate company ; has a depth of about 2.5m ; varied colours and offensive odour (Appendix 7)
LCA-EF1	Effluent	Ilupeju Industrial Estate	Canal with vegetation ; weeds at the edge, it is about 3.0m deep, coloured with offensive odour (Appendix 8)
LCA-EF2	Effluent	Ilupeju Industrial Estate	Canal with vegetation; weeds at the edge, it is about 3.0m deep, coloured with offensive odour
KJE-SD	Sediment	Ikeja Industrial Estate	collective effluent point ;Open sewer , marshy with vegetation
KHO-SD	Sediment	Ikeja Industrial Estate	metal company; open drainage
SVJ-SD	Sediment	Isolo Industrial Estate	food and beverage industry; open drainage
LPZ-SD1	Sediment	Ilupeju Industrial Estate	a conglomerate; open drainage
LPZ-SD2	Sediment	Ilupeju Industrial Estate	a conglomerate; open drainage
LPZ-SD3	Sediment	Ilupeju Industrial Estate	a conglomerate; open drainage
LCA-SD1	Sediment	Ilupeju Industrial Estate	canal with vegetation
LCA-SD2	Sediment	Ilupeju Industrial Estate	canal with vegetation

Table 3.2: contd.

Sample Code	Type of Sample	Location	Location Features
KBP-SL1	Topsoil	Ikeja Industrial Estate	roadside soil around paint company
KGI-SL2	Topsoil	Ikeja Industrial Estate	roadside soil around galvanizing company
KWS-SL3	Topsoil	Ikeja Industrial Estate	roadside soil around textile company
KMB-SL4	Topsoil	Ikeja Industrial Estate	roadside soil around pharmaceutical company
SJW-SL1	Topsoil	Isolo Industrial Estate	roadside soil around pharmaceutical company
SJW-SL2	Topsoil	Isolo Industrial Estate	roadside soil around pharmaceutical company
SJW-SL3	Topsoil	Isolo Industrial Estate	roadside soil around pharmaceutical company
SAF-SL4	Topsoil	Isolo Industrial Estate	roadside soil around pharmaceutical company
SAF-SL5	Topsoil	Isolo Industrial Estate	roadside soil around pharmaceutical company
SVJ-SL6	Topsoil	Isolo Industrial Estate	roadside soil food and beverage industry
K-CTR-SL1	Topsoil	Control soil for Ikeja Industrial Estate soil	residential area outside the estate ; open area with few houses
K-CTR-SL2	Topsoil	Control soil for Ikeja Industrial Estate soil	residential area outside the estate ;open area with few houses
S-CTR-SL1	Topsoil	Control soil for Isolo Industrial Estate soil	residential area outside the estate; open area with few houses
S-CTR-SL2	Topsoil	Control soil for Isolo Industrial Estate soil	residential area outside the estate; open area with few houses

3.3.3 Collection of Drainage Channel Sediment

Sediment samples were collected at a depth of 0-15cm using a clean hand trowel at the drainage channels. Samples were collected the sampling points as composites and were stored in polythene bags. The sediment samples were transported to the laboratory, and air-dried for 10-15days. Non-soil materials (such as wood, stones, and dirt) were removed by hand picking, and the samples then crushed manually, using porcelain mortar and pestle. The sediments were then sieved using a 2 mm mesh sieve, and stored in polythene bags for analysis.

Total number of sediments collected was: Ikeja Industrial estate - 20, Isolo Industrial Estate - 5, Ilupeju Industrial Estate - 47.

3.3.4 Collection of Soil

Soil samples were collected beside the effluent channels. These were obtained as composite samples and stored in polythene bags. They were treated in same manner as the sediment samples.

3.4 ANALYSIS OF EFFLUENT SAMPLES FOR PHYSICOCHEMICAL PARAMETERS

All analysis were carried out using standard procedures of the American Public Health Association (APHA-AWWA-WEF, 1998)

3.4.1 Determination of pH

pH was determined by electrometric method using a pH meter (Mettler Toledo, model MP 220). Buffer tablets were used to prepare buffer 4, 7 & 9. Each of the tablets was dissolved in 100mL of distilled water respectively. The pH meter was calibrated by alternatively dipping the electrode into buffer solutions of pH 4.00, 7.02 & 9.02

3.4.2 Determination of Conductivity

Conductivity was determined by electrometric method using a conductivity meter (Jenway, model 4076). The meter was calibrated with saturated solution of KCl to give a reading of 1420 µS/cm prior to use.

3.4.3 Determination of Total Dissolved Solids

Total Dissolved Solids was determined by electrometric method using a TDS meter (Jenway, model 4076).

3.4.4 Determination of Alkalinity

Alkalinity was determined by titrimetry method using methyl orange indicator.

Reagents:

Sodium carbonate, 0.1M Standard volumetric solution: anhydrous sodium carbonate (5.300 g) which have been dried,cooled in a dessicator, was weighed out dissolved in distilled water, and diluted to 1 litre in a volumetric flask.

Hydrochloric acid, 0.1M Standard volumetric solution: concentrated hydrochloric acid (10 mL) was added to distilled water and diluted to 1 Litre. The solution was standardized against 0.1M sodium carbonate, using methyl orange indicator.

Methyl orange indicator solution: methyl orange (1 g) was dissolved in distilled water and diluted to 1 Litre.

Phenolphthalein indicator solution: phenolphthalein dye (1.0 g) was dissolved in 100 mL ethanol (95%), and 100 mL of distilled water was added, and the mixture then stirred. The solution was stored in a reagent bottle and labeled.

Procedure:

Total Alkalinity: An aliquot of the sample (50-100 mL) was added 2 to 3 drops of methyl orange indicator solution was added. It was titrated with the standard acid from yellow to an orange colour end point.

Calculation:

$$\text{Total Alkalinity (mg/L) `}= \frac{\text{Vol. of 0.1M HCl x 5000}}{\text{Vol. of Sample (mL)}}$$

3.4.5 *Determination of Total Hardness,*

Total Hardness was determined by EDTA titrimetry procedure using solochrome black T indicator.

Reagents:

Buffer (pH 10): concentrated ammonium hydroxide (NH_4OH) (143 mL) was added to 16.9 g of ammonium chloride (NH_4Cl) and diluted to 250 mL with water.

Erichrome Black T Indicator: erichrome black T solid indicator (0.2 g) was dissolved in 15 mL of triethanolamine and 5mL of absolute ethanol.

Standard 0.01M EDTA Titrant: Sodium ethylenediaminetetraacetate dihydrate $Na_2H_2EDTA.2H_2O$ was dried at 80^{o}C for 1 hour and cooled in a dessicator. 3.723 g was accurately weighed and dissolved in water and diluted to 1000 mL. The solution was standardised against standard zinc sulphate solution. The solution was stored in polyethylene bottle.

Procedure:

Total hardness: 2 mL of pH 10 buffer was added to 50 mL of sample in a conical flask, followed by 2 drops of Eriochrome Black T, this was titrated with 0.01M EDTA from wine-red to blue colour end point. Blank was run in a similar way as sam ples, and values were subtracted from that of sample.

Calculation:

$$\text{Total hardness (mg CaCO}_3\text{/L)} = \frac{\text{Titre (mL)} \times 1000}{\text{Vol. of sample (mL)}}$$

3.4.6 Calcium and Magnesium

Calcium was determined by EDTA titrimetry procedure using calcon indicator after making the pH of sample solution sufficiently high that the magnesium is precipitated as hydroxide while Magnesium was determined by the difference in titre values between total hardness and calcium.

Reagents:

Sodium Hydroxide 1.0 M: sodium hydroxide (40.0 g) was dissolved in 1000 mL of water.

Solid Calcon Indicator.

Procedure

Calcium Hardness: 2 mL of NaOH solution or a volume sufficient to produce a pH of 12 to 13 was added to 50 mL sample in conical flask, followed by the addition of 0.1g of Calcon indicator. This was stirred, and titrated with 0.01M EDTA with continuous stirring to a blue end- point. Blank was run in a similar way as samples, and values were subtracted from that of sample.

Calculations:

$$\text{Conc. of Ca (mg/L)} = \text{Titre} \times \text{Molarity of EDTA} \times 40 \times \frac{1000}{\text{Vol. of Sample (mL)}}$$

$$\text{Conc. of Mg (mg/L)} = \text{Titre} \times \text{Molarity of EDTA} \times 23 \times \frac{1000}{\text{Vol. of Sample (mL)}}$$

3.4.7 Determination of Chloride

Chloride was determined by titrimetrically with mercuric nitrate reagent and diphenylcarbazone indicator.

Reagents:

Hydroquinone solution: hydroquinone (1.0 g) was dissolved in 100 mL of water. The solution was freshly prepared when needed.

Nitric acid, approximately 0.05 N: concentrated nitric acid (3.2 mL) was diluted to 1 Litre.

Sodium hydroxide, approximately 0.05 M: sodium hydroxide (2 g) was dissolved in water and diluted to 1 Liter.

Mercury (II) nitrate standard solution: mercury (II) nitrate, $Hg(NO_3)_2.H_2O$, (5.04 g) was dissolved in 50 mL of water containing 0.5 mL of concentrated nitric acid, diluted to 1L and filtered. This solution was standardized against 25 mL of sodium chloride standard solution, and adjusted so that

$$1.0 \text{ mL} \equiv 1.0 \text{ mg } Cl^-$$

The solution was stored in a brown bottle.

Sodium chloride standard solution: sodium chloride, NaCl (1.648 g) dried, cooled in a dessicator was dissolved in water and diluted to 1 Litre, so that

$$1.0 \text{ mL} \equiv 1.0 \text{ mg } Cl^-$$

Indicator solution: diphenylcarbazone (0.5 g) and bromophenol blue (0.05 g) were dissolved in 100 mL of ethanol (95% v/v) and stored in a brown bottle.

Procedure:

A measured volume (V) of sample was placed in a conical flask and diluted or evaporated down as necessary to about 50 mL. 5 mL of hydroquinone solution was added to mask chromate and iron (III) ions. Five to ten drops of indicator solution was added. If a blue, blue violet or red colour developed, 0.05 M nitric acid was added drop wise until the colour changes to yellow and 1mL in excess was added. If a yellow or orange colour developed 0.05M sodium hydroxide was added until the colour changed to blue violet and 0.05 M nitric acid was added until the colour changed to yellow, and then 1mL in excess was added. Mercury (II) nitrate standard solution was then titrated against the solution. Blank correction was carried out by titrating against 50 mL of distilled water.

Calculation:

$$\text{Concentration of chloride (mg/L)} = \frac{(V_1 - V_2) \times 1000}{V}$$

V_1 = Volume (mL) of mercury (II) nitrate solution required for sample.

V_2 = Volume (mL) of a mercury (II) nitrate solution required for blank.

V = Volume (mL) of sample taken.

3.4.8 Determination of Sulphate

Sulphate was determined by the turbidimetric method involving the precipitation of sulphate ions as barium suphate and stabilisation with conditioning reagent.

Reagents:

Barium chloride crystals:

Conditioning reagent: 75 g of sodium chloride, 30 mL of concentrated hydrochloric acid, 100 mL of 95% propan-2-ol and 50 mL of glycerol were dissolved in 300 mL of water, and mixed well.

Sulphate standard solution: anhydrous sodium sulphate (0.1479 g) was dissolved in I L of distilled water.

$$1.0 \text{ mL} = 100\ \mu\text{g } SO_4^{2-}$$

Procedure:

Preparation of calibration graph : Appropriate amount of sulphate standard solution was measured into 100 mL volumetric flasks to cover the range up to 10..0 mg SO_4^{2-} (0.5, 1, 2, 3, 4, 6, 8 and 10 mg SO_4^{2-}) and the solutions were made up to 50 mL with water. Sulphate determination was continued according to the procedure described below, and a blank simultaneously carried out.

Treatment of test and blank solutions: A quantity (50 mL) of sample was measured into 250 mL beaker. 5 mL of the conditioning reagent was added and the mixture stirred with a magnetic stirrer at a constant speed. While the solution was being stirred, about 0.5 g of barium chloride crystals was added, and the stirring continued for exactly one minute at the same speed. Immediately after one minute the absorbance was measured at 420 nm wavelength using double beam uv/visible cecil 3025 spectrophotometer The readings were taken at intervals of 30 seconds over a period of four minutes, and the maximum reading was recorded. Typical calibration graph obtained is given in Appendix 9. The number of µg of sulphate in the sample was estimated from calibration curve, and the concentration calculated as:

$$\text{Conc. of } SO_4^{2-}\ (\text{mg/L}) = \frac{\text{No of mg } SO_4^{2-} \text{from calibration extrapolation}}{\text{Volume of Sample (mL)}}$$

3.4.9 *Determination of Phosphate*

Phosphate was determined by the colorimetric method involving the reaction of phosphate ions with ammonium molybdate and potassium antimony tartarate in acid medium to form phosphomolybdic acid. This is then reduced to intensely coloured molybdenum blue complex with ascorbic acid.

Reagents:

Sulphuric acid, approximately 10M: concentrated sulphuric acid (139 mL) was carefully added to water. The mixture was cooled and diluted to 1000 mL.

Ammonium molybdate solution: ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}.4H_2O$ (40 g) was dissolved in 1000 mL distilled water and stored in a glass-stoppered bottle.

Ascorbic acid solution 0.01M: ascorbic acid (3.4 g) was dissolved in 200 mL water. This solution was stable for just one week at 4 ^{o}C.

Potassium antimonyl tartarate solution: potassium antimonyl tartarate, $K(SbO)C_4H_4O.½H_2O$, (2.743 g) was dissolved in 1000 mL water and stored in a glass-stoppered bottle.

Stock phosphate solution: anhydrous potassium dihydrogen phosphate, KH_2PO_4, (219.5 mg) was dissolved in water and diluted to 1000 mL.

$$1.0 \text{ mL} \equiv 50 \text{ µg } PO_4^{3-}$$

Phosphate working solution: 5 mL of the stock phosphate solution was diluted to 500 mL with water.

$$1.0 \text{ mL} \quad 2.5 \text{ µg } PO_4^{3-}$$

Combined reagent: The above reagents were mixed to obtain 500 mL combined reagent: 250 mL of 10M sulphuric acid, 75 mL of ammonium molybdate solution, 25 mL of potassium antimonyl tartarate, 150 mL of ascorbic acid solution. At each addition, the combined reagent was properly mixed and allowed to reach room temperature. The reagent was stable for 4 hours.

Procedure

Preparation of calibration graph: Accurately measured amounts of phosphate working solution covering the range of 1 to 15 µg PO_4^{3-} were placed in stoppered 50 mL volumetric flask. These were diluted as necessary to 40 mL of distilled water. 40 mL of distilled water was placed in another flask for use as blank. The process was continued according to the procedure described below.

Treatment of test and blank solution: A sample solution of 40 mL was placed into a 50mL stoppered volumetric flask while 40 mL of distilled water as blank was placed in another flask. 8 mL of the combined reagent was added and the content mixed and diluted to 50 mL with distilled water. These were allowed to stand for 10 minutes, and the absorbance measured at 880nm with a double beam uv/visible spectrophotometer (Cecil 3025). Typical calibration graph obtained is given in Appendix 10. The number of µg of phosphate in the sample was estimated from calibration curve, and the concentration calculated as:

$$\text{Conc. of } PO_4^{3-} \text{ (mg/L)} = \frac{\text{No of mg } PO_4^{3-} \text{ from calibration extrapolation}}{\text{Volume of Sample (mL)}}$$

3.4.10 Determination of Nitrate

Nitrate was determined by phenoldisulphonic acid method (Marczenko, 1986). The nitration of 2, 4-phenoldisulphonic acid forms 6-nitrophenol-2, 4-disulphonic acid which, on subsequent addition of ammonium hydroxide solution produces a yellow coloured compound.

Reagents:

Phenoldisulphonic acid: solution in concentrated H_2SO_4: phenol (12.5 g) was dissolved in 75 mL of concentrated H_2SO_4, 37.5 mL of 13 % oleum added and the mixture was stirred well. The solution was heated in 250 mL conical flask for 2 hours on a boiling water-bath with occasional stirring.

Stock nitrate solution: potassium nitrate, KNO_3, 0.7128 g which has been dried, cooled in a desiccators, was weighed out, dissolved in distilled water and diluted to 1000 mL. The solution was preserved with 2 mL chloroform per litre.

$$1.0\ \text{mL} \equiv 100\ \mu g\ NO_3^- \text{-N}$$

Nitrate working solution: 25.0 mL of the stock nitrate solution was diluted to 500 mL with distilled water.

$$1.0\ \text{mL} \equiv 5.0\ \mu g\ NO_3^- \text{-N}$$

Silver sulphate solution: silver sulphate (1.10 mg) was dissolved in 250mL of distilled water.

$$1.0\ \text{mL} \equiv 1.0\ \text{mg of}\ Cl^-$$

Calcium carbonate suspension: $CaCO_3$ (1.0 g) was mixed with 100 mL of distilled water.

Procedure:

Preparation of calibration graph: Standards were prepared to cover 0, 5, 10, 20, 30, 40 and 50μg NO_3^-N / 50 mL by diluting 0.0, 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0mL of the standard nitrate solution to 50mL with distilled water in a volumetric flask. Blank was also prepared using only 50mL of distilled water and the determination of NO_3^- -N was carried out as described below. The standards were treated in the same manner as samples. A calibration graph of absorbance of the standards against number of microgram of NO_3^--N / 50 mL was constructed.

Treatment of test and blank solutions: High chloride causes low results owing to the reaction between HCl and HNO_3 when the phenoldisulphonic acid in concentrated sulphuric acid is added to some samples;

$$3Cl^- + NO_3^- + 4H^+ \rightarrow Cl_2 + NOCl + 2H_2O$$

Large amount of chloride was precipitated as AgCl and filtered beforehand by the addition of slightly less than stoichiometric quantity of silver sulphate to the sample. 50 mL of sample was measured into a 100 mL beaker, neutralised by the addition of 1 mL of $CaCO_3$ suspension and evaporated to dryness in a water bath at 105 °C.The cooled residue was treated with 2mL of phenoldisulphonic acid reagent and stirred well. After 5 minutes, it is diluted with 10mL of water and transferred quantitatively to a 50 mL standard flask. Concentrated ammonia solution was added until the solution became intensely golden yellow, then 2 mL was added in excess and diluted to mark with distilled water. The absorbance of the golden yellow colour was measured at 410nm with a double beam uv/visible cecil 3025 spectrophotometer. Typical calibration graph obtained is given in Appendix 11. Number of mg of nitrate in the sample was estimated from calibration curve, and the concentration calculated as:

Calculation:

$$\text{Conc. } NO_3^- \text{ (mg/L)} = \frac{\text{No of mg } NO_3^- \text{ from calibration extrapolation}}{\text{Volume of Sample (mL)}}$$

3.5 ANALYSIS OF EFFLUENT SAMPLES FOR HEAVY METALS

Sample of 200 mL was measured into a 500 mL beaker, and 5 mL of concentrated nitric acid was carefully added. This solution was concentrated to 20 mL by heating on a water bath for few hours. The concentrated extract was cooled and transferred into a 50 mL standard flask, then made up to mark with distilled water. Heavy metal (Pb, Cd, Zn, Cu, Cr and Ni) contents of the samples were determined using atomic absorption spectrophotometer (Perkin Elmer, Model AAnalyst 200, Waltham, USA) involving direct aspiration of the aqueous solution into air-acetylene flame. Table 3.3 gives the detailed information on the atomic absorption spectrophotometer operating conditions and the range of standards for each metal. . A reagent blank was prepared and analysed. Heavy metal concentrations of a series of standards (BDH)were determined and a calibration graph constructed. From the graph the concentrations of heavy metals in the sample were calculated.

Calculation:

$$\text{Conc. (mg/L)} = \frac{\text{Conc. from AAS (mg/L)} \times \text{Vol. of extract (mL)}}{\text{Vol. of sample (mL)}}$$

3.6 ANALYSIS OF EFFLUENT SAMPLES FOR GROSS ORGANIC POLLUTANTS

All analysis were carried out using standard procedures of American Public Health Association (APHA-AWWA-WPCF, 1998).

Table 3.3: Operating conditions for the atomic absorption spectrophotometer.

Element	**Wavelength (nm)**	**Slit Width (nm)**	**Lamps Current (mA)**	**Flame Type**	**Range of Working Standards (mg/L)**
Pb	283.3	2.7	10	Air-C_2H_2	0-10
Cd	228.8	2.7	4	Air-C_2H_2	0-1
Zn	213.9	2.7	15	Air-C_2H_2	0-1.6
Cu	324.8	2.7	15	Air-C_2H_2	0-6.4
Cr	357.9	2.7	25	Air-C_2H_2	0-6.4
Ni	232.0	1.8	25	Air-C_2H_2	0-4

Source: Perkin Elmer (2007).

3.6.1 Determination of Dissolved Oxygen.

Dissolved oxygen was determined by Winkler's Method. This method is based on the addition of manganous sulphate solution and alkali-iodide-azide solution to the water sample. This results in the formation of manganous hydroxide precipitate. Any dissolved oxygen present in sample solution then rapidly oxidizes an equivalent amount of the dispersed manganous hydroxide precipitate to form higher hydroxide. Subsequent acidification of this solution liberates iodine in an amount chemically equivalent to the original dissolved oxygen content of the sample. The iodine is then determined by titration with a standard solution of sodium thiosulphate

Reagents:

Alkaline iodide solution: sodium hydroxide (400 g) was dissolved in 560 mL of water, after which 90 g of sodium iodide was added and the solution kept hot until the iodide had completely dissolved. The solution was cooled and diluted to 1 Litre. No iodine was liberated when 1 mL is diluted to 50 mL and acidified.

Alkaline iodide-azide solution: alkaline iodide solution (1 Litre) was mixed with 300mL of 2.5% sodium azide solution.

Concentrated sulphuric acid

Manganese (II) sulphate solution: hydrated manganese (II) sulphate, $MnSO_4.5H_2O$, (500 g) was dissolved in water, filtered and made up to 1 Litre.

Potassium iodate, 0.025M : Potassium iodate was dried at 120^o C for 2 hours, cooled in a dessicator, 0.892 g was weighed out, dissolved in water and diluted to 1 Litre. The solution was stored in a glass-stoppered bottle.

Sodium thiosulphate, approximately 0.025M: sodium thiosulphate pentahydtate, Na $_2S_2O_8.5H_2O$, (6.3g) was dissolved in 1 Litre of copper- free water, 1mL of chloroform was added to stabilize the solution. This was stored in a brown bottle.

Sodium thiosulphate working solution: The 0.025M sodium thiosulphate solution was diluted to strength of 0.0125M. For standardization, 10 mL of 0.025M potassium iodate was measured by pipette into a conical flask containing 100 mL water and 1mL of potassium iodide solution was added, followed by 2 mL of conc. sulphuric acid. The content was mixed thoroughly, and then titrated with the 0.0125M thiosulphate, adding 2mL of starch solution just before the end point.

Sampling:

Glass bottles (250 mL capacity) with narrow neck and well-fitted ground-glass stoppers were used for sampling. These sampling bottles were cleaned with 5M sulphuric acid and then rinsed thoroughly with water. Synthetic detergent was used for cleaning. The bottles were subsequently kept clean by acidic iodine solution of the Winkler procedure and required no further treatment apart from thoroughly rinsing with tap water before use. For the purpose of sampling industrial effluent and canal water, the sampling bottles were held horizontally at the surface so that the water enters gently, without bubbling. As the bottle fills, it was brought gradually to the vertical position. Finally the Winkler reagent was added immediately the sample was taken, as changes in the concentration of dissolved oxygen may occur rapidly.

Procedure:

To the sample, 1 mL of manganese (II) sulphate solution was added well below the surface of the liquid and 1 mL of alkaline-iodide-azide solution was added at the surface. The stopper was carefully replaced so as to avoid inclusion of air bubbles, and the content thoroughly mixed by inverting and rotating the bottle several times. When the precipitate had settled to the lower third of the bottle, the mixing was repeated and the precipitate allowed to settle completely leaving a clear supernatant liquid. 2 mL of concentrated sulphuric acid was added with measuring cylinder. The stopper was replaced and the content thoroughly mixed by rotation. A 100 mL of the solution was measured into a conical flask and the iodine immediately titrated with standard thiosulphate solution, while 2 mL of starch indicator solution was added towards the end of the titration.

Calculation:

$$\text{Dissolved oxygen conc. (mg/L)} = \frac{\text{Volume of 0.0125M thiosulphate (mL)} \times 101.6}{\text{Volume of sample titrated (mL)}}$$

3.6.2 Determination of Biochemical Oxygen Demand (BOD_5)

Biochemical Oxygen Demand (BOD_5) was determined by Dilution Method. 250 mL glass bottles with narrow neck and well-fitted ground-glass stoppers were used. These bottles were cleaned with 5 M sulphuric acid and then rinsed thoroughly with water. Synthetic detergents were used for cleaning.

Reagents:

Dilution water: Stock solutions of the following pure chemicals are required.

Calcium Chloride solution: calcium chloride, $CaCI_{2,}$ (27.5 g), was dissolved in 1Litre of water.

Iron (III) chloride solution: iron (III) chloride hexahydrate, $FeCl_3.6H_2O$, (0.125 g), was dissolved in 1 Litre of water.

Magnesium sulphate solution: magnesium sulphate heptahydrate, $MgSO_4.7H_2O$, (25 g), was dissolved in 1 Litre of water.

Phosphate buffer stock solution: potassium dihydrogen phosphate, $KH_2PO_{4,}$ (42.5 g) was dissolved in 700 mL of water, and 8.8 g of sodium hydroxide was added. 2 g of ammonium sulphate was added, and diluted to 1 Litre.

To every Litre of freshly distilled water, 1 mL of each reagent was added. The water was taken to incubation temperature and saturated with oxygen by bubbling air through it for forty eight hours, and the water used soon after saturation.

Procedure:

Preliminary treatment of sample: for pH of the sample that was not between 6.5 and 8.5, sufficient alkali or acid was added to bring it within the range. The amount of acid or alkali added is determined on a separate sample.

Dilution of sample: With some samples more than one dilution was carried out. For example: industrial effluents vary so much in character that no limits of dilution can be suggested. A range of dilution, for example 1 : 5, 1:15, 1:50, 1:150, was carried out and the best dilution that gave at least 30% of the oxygen remaining after 5 days was used. Samples which were stored in a refrigerator were allowed to reach room temperature before dilutions were made. The following principles were strictly adhered to in preparing the dilutions:

(i) The sample and dilution water was mixed thoroughly but violent agitation leading to the formation of minute air bubbles was avoided. Mixing was accomplished by careful repeated inversion of a measuring cylinder containing the sample and dilution water.

(ii) The diluted mixture were transferred to two incubator bottles (or more when replicate results were required) by careful pouring. Exactly the same mixing and transfer mixing technique was used for all samples.

(iii) Bottles of the dilution water used in the test were prepared at the same time as the sample dilution to permit determination of the blank.

Carrying out the test: The initial concentration of dissolved oxygen in one bottle of the mixture of sample and diluted water, and in one of the bottles containing only dilution water was determined immediately. The other bottles (those containing the mixture of sample and dilution water, and that containing the plain dilution water to act as a blank) were placed in the dark at room temperature. After 5 days, the dissolved oxygen in the diluted sample and the blank was determined. In both case, the azide method described for dissolved oxygen determination was used.

Calculation:

$$\text{BOD content (mg/L)} = \frac{(x\text{-}y\text{-}az)}{a+1}\frac{(a+1)}{2}$$

Where:

x = volume of 0.0125 M thiosulphate required for 100mL of the original dilution (mL)

y= volume of 0.0125 M thiosulphate required for 100mL of incubated dilution (mL)

a = volume of diluted water to 1 volume of sample (mL)

z = difference between volumes of 0.0125 M thiosulphate requires for 100mL of dilution water before and after incubation (mL). (The blank correction).

3.6.3 Determination of Chemical Oxygen Demand

Chemical Oxygen Demand was determined by the method of oxidation with potassium dichromate, followed by titrimetric determination of the unreacted dichromate with iron (II) sulphate heptahydrate.

Reagents:

Iron (II) sulphate, 0.125 M: iron (II) sulphate heptahydrate, $FeSO_4.7H_2O$, (34.75 g) was dissolved in 100mL of 1:3 diluted sulphuric acid , and diluted to 1 Litre.

Potassium dichromate, 0.125 M: potassium dichromate, $K_2Cr_2O_7$, (6.129 g) was dissolved in water and diluted to 1 Litre.

Iron (II)-1, 10-phenanthroline indicator solution: iron (II) sulphate heptahydrate, $FeSO_4.7H_2O$, (3.475g) was dissolved in 500 mL of water. To this was added 7.427 g of 1,10-phenanthroline monohydrate and the mixture was shaken until dissolved.

Silver sulphate solution: silver sulphate (1.25 g) was dissolved in 100mL 1:1 sulphuric acid solution.

Sulphuric acid: concentrated.

Procedure:

10 mL of 0.125 M potassium dichromate was accurately measured and transferred with 30mL of concentrated sulphuric acid into a 250 mL round bottom flask and mixed well. The flask was cooled in a tray containing cold water, 1 mL of silver sulphate solution was added followed by 20mL of sample and few anti-bumping granules are added. The flask was fitted to the reflux condenser and boil under reflux for two hours. The content was allowed to cool, and 60 mL of distilled water was added and the content was allowed to cool. A drop of indicator solution was added and the residual dichromate was titrated with 0.125M Iron (II) sulphate added from a burette. A blank determination was carried out in a similar way using 20mL of distilled water instead of sample.

The sample titration is subtracted from the blank titration to give the volume of potassium dichromate equivalent to the oxygen demand.

Since 1.0 mL of 0.125 M potassium dichromate = 1.0mg of oxygen

Calculation:

$$\text{COD (mg/L)} = \frac{\text{Blank titre (mL)} - \text{sample titre (mL)} \times 1000}{\text{Volume of sample titrated (mL)}}$$

3.7 ANALYSIS OF SEDIMENT FOR PHYSICOCHEMICAL PARAMETERS

The following parameters were determined in sediment: pH, organic carbon, particle size distribution (i.e., mechanical properties) and heavy metals (Pb, Cd, Zn, Cu, Cr and Ni).

The analyses were carried out using standard procedures.

3.7.1 Determination of Sediment pH

pH was determined by electrometric method (Page,1982), using pH meter (Mettler Toledo, model MP 220). The pH meter was calibrated as stated in 3.4.1

Procedure:

Sediment samples were sieved (2 mm mesh), dried in an oven at 105°C for 4 hrs, and cooled in a desiccator. 20 g of the dry sample was weighed into a 50 mL plastic container. 20 mL of deionised water was added and the mixture was allowed to stand for 30 minutes with occasional stirring, using a glass rod. After calibration of the pH meter, the pH of the sediment suspensions, were taken using the pH meter. The electrode was rinsed with deionised water and wipe with a dry tissue paper after each reading.

3.7.2 Determination of Sediment Particle Size Distribution

Particle size analysis was done by Bouyoucos hydrometer method (Gee and Bauder, 1979)

Reagent:

Sodium hexametaphosphate dispersing agent (5%): sodium hexametaphosphate (50 g) was weighed and dissolved in 1000 mL water.

Procedure:

50.0g of 2mm sieved air-dried sediment was weighed into a 400mL beaker. 50 mL of 5.0% sodium hexametaphosphate was added along with 100 mL of water. The suspension was stirred and allowed to stand for 20 minutes, then stirred again for 15 minutes with a mechanical shaker. After the shaking, the suspension was transferred to a glass cylinder. With the hydrometer in the suspension, water was added making the volume of water to be 1000 mL. The cylinder was covered with a tight fitting rubber bung and the suspension was mixed by inverting the cylinder carefully. The cylinder was place on a flat surface and the time noted. The hydrometer was gently placed immediately into the cylinder and after 40 seconds the first hydrometer and temperature readings of the suspension were taken (H_1 and T_1).

After this the cylinder was allowed to stand for three hours and the second hydrometer and temperature readings were taken (H_2 and T_2). The first reading measures the percentage of silt and clay in suspension. The second reading indicates the percentage of 2- micron (total) clay in the suspension. Results were corrected to a temperature of 68^o F. For every degree over 68^o F, 0.2 are added to hydrometer reading before computation and for under 68^o F, 0.2 was subtracted from hydrometer reading. 2.0 are subtracted from every hydrometer reading to compensate for the added dispersing agent.

Calculation:

% Sand = $100.0 – [H_1 + 0.2 (T_1 -68) – 2.0]2$

% Clay = $[H_2 + 0.2 (T_2 – 68)2]$

% Silt = 100.0 – (% sand + % clay)

3.7.3 Determination of Organic Carbon Content of Sediment

Organic Carbon was determined by the method of Nelson and Sommers (1996). The method measures the amount of degradable organic matter in sediment and soil. Sediment and soil organic carbon is almost completely oxidized with potassium dichromate ($K_2Cr_2O_7$) in the presence of H_2SO_4, leaving the fraction present in inorganic form. The excess dichromate is determined by titration with ferrous sulphate

Reagents:

Potassium dichromate ($K_2Cr_2O_7$) 6M: potassium dichromate (49.04 g) was dissolved in water and diluted to 1000 mL.

Ferrous sulphate 0.5 M: ferrous sulphate heptahydrate, $FeSO_4.7H_2O$, (140 g) was dissolved in 300 mL of water containing 15 mL of concentrated sulphuric acid, and diluted to 1000 mL. This solution was standardized before use by titrating against 10 mL 6 M $K_2Cr_2O_7$.

Concentrated sulphuric acid.

O-phenanthroline- ferrous complex 0.025M (ferroin): Ferroin indicator was prepared by dissolving 14.85 g of O-phenanthroline monohydrate and 6.95 g of $FeSO_4.7H_2O$ in water, and diluting to 1000 mL.

Procedure:

1.00 g of sieved sediment samples was weighed in duplicate and transferred to 250 mL Erlenmeyer flasks. 10 mL of 6M $K_2Cr_2O_7$ solution was pipetted into the flask, and the flask was swirled gently to disperse the soil/sediment. 20 mL of concentrated H_2SO_4 was rapidly added and the flask immediately swirled gently until soli/sediment and reagents were mixed. The flask was allowed to stand on a sheet of asbestos for about 30 minutes. 100 mL of distilled water was added after standing for 30 minutes. 3-4 drops of ferroin indicator was added and titrated with 0.5 M ferrous sulphate solution. As the end point was approached, the solution takes on a greenish cast and then changes to dark green. At this point, the ferrous sulphate was added drop by drop until the colour changed sharply from blue to red (maroon colour) in reflected light against a white background. The blank titration was made in a similar way but without sediment, to standardize the dichromate.

Calculation:

$$\%\ \text{Organic carbon} = \frac{\text{me } K_2Cr_2O_7 \text{ -me } FeSO_4 \times 0.03 \times 100 \times (f)}{\text{Mass (g) of air-dry sediment}}$$

Correction factor, f = 1.33

me = molarity of solution x volume (mL) of solution used

% Organic matter in soil/sediment = % Organic carbon x 1.729

3.8 DETERMINATION OF METALS IN SEDIMENT

Heavy metals were determined by atomic absorption spectrophotomettry of wet-digested samples.

Reagents:

Nitric acid, 2 M: Concentration nitric acid (127 mL) was accurately measured into 1000 mL volumetric flask which contained 200 mL of water. The mixture was made up to mark with distilled water.

Procedure:

Sieved air-dried sediment (5.0 g) was weighed into 250 mL beaker; 50 mL of 2 M nitric acid was measured and added to the sediment sample. The mixture was swirled gently and the content boiled on a water bath with a watch glass lid for 50 minutes. On cooling, the extract was filtered through Whatman No. 1 filter paper into a clean 50ml standard flask. A reagent blank was also prepared. Heavy metals (Pb, Cd, Zn, Cu, Cr and Ni) were determined using an atomic absorption spectrophotometer as previously described in section 3.5.

Calculation:

$$\text{Metal concentration } (\mu g/g) = \frac{(A - B) \times V}{W}$$

A = concentration (µg /mL) of metal in the sample from AAS reading

B = concentration (µg /mL) of metal in the blank from the AAS reading

W = Weight (g) of soil sample used for extraction

V = Volume (mL) of the extract used

3.9 ANALYSIS OF SOIL

The following parameters were determined in soil: pH, organic carbon, particle size distribution or Mechanical properties and heavy metals (Pb, Cd, Zn, Cu, Cr and Ni). The analyses were carried out as described for sediment (Sections 3.7 and 3.8).

3.10 CHEMICAL TREATMENT OF TEXTILE EFFLUENT.

The study is about the use of flocculation/ coagulation method in the treatment of industrial effluents. From the results obtained from the effluent characterisation study, it was noted that the most highly organically polluted effluents were those obtained from the textile and pharmaceutical industries with extreme values of BOD and COD. The textile industry effluents were then selected for testing the efficiencies of a variety of treatment methods for the reduction of the organic load. Effluent generated from Woolen and Synthetic Textile Manufacturing Limited located in Ikeja Industrial Estate was collected from the discharged channel with aid of pre washed polyethene container into pre washed 25 Litre plastic containers. The sample was transported to the laboratory. The pH, TDS, TSS, COD, and Conductivity were determined on the sample prior to treatment. TDS will give an idea of the level of inorganic components in the effluent. COD indicates the level of organic load in the effluent; TSS will give the level of suspended solutes, while conductivity indicates the levels of dissolved solutes. The monitoring was done for 30 days in order to establish the optimum results for the parameters monitored.

The following categories of treatment options were employed:

(a) **Application of Fenton's reagent**

- $FeCl_2 .4H_2O + H_2O_2$,
- $FeSO_4.7H_2O + H_2O_2$
- $FeCl_2 .4H_2O + FeSO_4.7H_2O + H_2O_2$

(b) **Application of Inorganic Coagulants.**

- $FeCl_2.4H_2O$
- $FeSO_4.7H_2O$,
- $FeCl_3$
- Alum

(c) **Application of other materials for treatment**

- Activated charcoal.
- Sunlight
- Darkness

3.10.1 Effluent Treatment Procedures

Coagulation studies were performed by the jar test. Twelve jars test were used and were labeled appropriately with the concentration and type of coagulant used. Into each of the jar was added 1L volume of effluent from the textile industry with known initial pH, TDS, TSS and COD concentration. The jars were labeled 1- 12, and into each of the jar were added the following amount concentrations of coagulant:

Jar 1 →Only the effluent sample, kept in the sunlight (No coagulant)
Jar 2 →Only the effluent sample, kept in the Dark (No coagulant)
Jar 3 → 1000 mg $FeCl_2 .4H_2O$
Jar 4 → 1000 mg $FeCl_2 .4H_2O$ + 10 cm^3 of H_2O_2
Jar 5 → 1000 mg $FeSO_4.7H_2O$
Jar 6 → 1000 mg $FeSO_4.7H_2O$ +10 cm^3 H_2O_2
Jar 7 → 500 mg each of $FeCl_2 .4H_2O$ + $FeSO_4.7H_2O$
Jar 8 → 500 mg each of $FeCl_2 .4H_2O$ and $FeSO_4.7H_2O$ + 10 cm^3 of H_2O_2
Jar 9 → 1000 mg $FeCl_3$
Jar 10 → 1000 mg Alum
Jar 11 → 1000 mg Charcoal
Jar 12 → Control.

Each of the jar was shaken for 1hour at 225 rev/ mm with Gallenkamp orbital shaker after which the samples were analysed for pH, TDS, TSS and COD. The samples were monitored for 30 days at various times intervals. pH , TDS, and COD were monitored daily for the first 14 days while subsequently, monitoring was done in once in two days for the rest of the treatment period. TSS was monitored for three days intervals for the period of treatment.

3.10.2: Analysis of the Parameters Determined in the Treated Effluent.

- Determination of pH: as described in section 3.4.1
- Determination of conductivity: as described in section 3.4.2
- Determination of COD: as described in section 3.6.3
- Determination of TSS: Total suspended solids in the treated samples were determined gravimetrically by evaporating 20 ml of treated samples in a pre-weighed evaporating dish at 110°C and expressing it in mg/L.

The removal efficiency (% Removal) was calculated from the following formula:

$$\text{COD reduction (\%)} = \frac{(C_o - C)}{C_o}$$

Where, C_o is initial COD value before treatment,

C is the COD value after treatment.

3.11 QUALITY CONTROL/QUALITY ASSURANCE (QC/QA)

3.11.1 General Quality Control.

The following general quality control measures were carried out throughout the course of this research:

- Sampling containers were properly cleaned with 2M HNO_3 acid and washed with plenty of distilled water.
- Analytical grade reagents were used.
- Certified Reference material GLAURM, an urban soil secondary material prepared by participants in the EU URBSOIL project (Davidson et al., 2006) was analysed.
- Effluent samples were kept at 4 ^oC and were allowed to assume room temperature before analyses were done.

3.11.2 Recovery Study

Recovery study was carried out on selected soil (six samples)/sediment (seven samples) based on the average levels of metals in the samples. This involved spiking of a previously analysed soil /sediment sample with a calculated amount of analyte standard and reanalyzing the spiked sample following the same method and procedure used for the unspiked soil/sediment sample to determine the percentage of the added standard that can be recovered. A total of five soils and two sediments samples were used and spiked with standard solutions of Pb while one soil and five sediments samples were used and spiked with standard solutions of Cd.

Procedure:

5.0 g of the previously analysed soil/sediment was weighed into a crucible.1 mL of the working standard solution was spiked on the cone soil/sediment inside the crucible and this was dried in the oven at 105^oC for one hour. The soil/sediment was then cooled in a dessicator and homogenized using a glass rod. 1.0 g of the homogenized soil/sediment was weighed out and digested as described in Section 3.8. The sample was digested, was then analysed for metals as previously described.

Calculation:

$$\text{Recovery}(\%) = \frac{\text{Result of re-analysis} - \text{original sample conc.} \times 100}{\text{increased conc. achieved by spiking}}$$

Comment of the Obtained Recovery Values:

The mean percentage recoveries were 92±13 for Pb and 86.1±8.5 for Cd as presented in Tables 3.4 and 3.5 respectively, are indicative of a high degree of accuracy in the analyses.

3.11.3 Analysis of Standard Reference Material

Reagents:

Aqua-regia acid mixture: concentrated hydrochloride acid, (300 mL) about 36% m/m (11 N) was carefully mixed with 100mL of concentrated nitric acid at a ratio of 3:1 in a 500mL reagent bottle.

Procedure:

1.0 g of GLAURM reference standard material was weighed into 250 mL beakers. 10mL of aqua regia was measured and added to the standard sample. The mixture was swirled gently, and the content boiled on a water bath with a watch glass lid for 50 minutes. On cooling, the extract was filtered through Whatman No. 1 filter paper into a clean 50 mL standard flask. The content was made up to mark with water, and stored for determination of heavy metal concentration using atomic absorption spectrophotometer. A reagent blank was carried out in the similar way but without sample. The values obtained are compared with the reference values in Table 3.6

Table 3.4: Results of recovery study for lead.

Sample Code	**Original Sample Concentration (µg/g)**	**Mass of Sample Taken (g)**	**Concentration of Standard Spiked (µg/mL)**	**Volume of Standard Spiked (mL)**	**Increased Concentration Achieved (µg/g)**	**Total Conc. Expected by Analysis (µg/g)**	**Result of Re-analysis (µg/g)**	**% Recovery**	**Mean % Recovery**
LPZ-SL2 (7)	129	5.0	750	1.0	150	279	253	82.7	92±13
SJW.SL^{-}(3)	44.4	5.0	250	1.0	50	94.4	97.7	107	
SAF-SL4(4)	27.0	5.0	150	1.0	30	57.0	57.3	101	
KHO-SD(9)	328	2.5	750	1.0	300	628	592	88	
KHO-SD(7)	262	2.5	750	1.0	300	562	491	76.3	
SJW-SL1(7)	13.2	5.0	75	1.0	15	28.2	25.5	82	
SJW-SL2(8)	3.21	5.0	25	1.0	5	8.21	8.5	106	

Table 3.5: Results of recovery study for cadmium

Sample Code	**Original Sample Concentration (µg/g)**	**Mass of Sample Taken (g)**	**Concentration of Standard Spiked (µg/mL)**	**Volume of Standard Spiked (mL)**	**Increased Concentration Achieved (µg/g)**	**Total Conc. Expected by Analysis (µg/g)**	**Result of Re-analysis (µg/g)**	**% Recovery**	**Mean % Recovery**
KJE-SD(6)	10.6	5.0	50	1.0	10	20.6	18.4	72	86.1±8.5
LPZ-SD2(7)	1.00	5.0	5	1.0	1	2.00	1.81	81	
LCA-SD1(10)	1.02	5.0	5	1.0	1	2.02	1.92	90	
KJE-SD(9)	14.6	5.0	75	1.0	15	29.6	27.5	86	
KJE-SD(10)	23.2	5.0	125	1.0	25	48.2	47.1	95.6	
KWS-SL5(10)	2.30	5.0	25	1.0	5	7.3	6.9	92	

Table 3.6: Results of analysis of standard reference material (GLAURM)

Metals	**Measured Concentrations** (µg/g)	**Certified Reference Values** (µg/g)
Pb	440	389±25
Cd	1.0	<0.74
Zn	165	117±11
Cu	117	111±5
Cr	54	43.2±3.0

Comment of the Obtained Reference Standard Values:

Student t-test ($t_{cal.}$= 2.045; t_{tab} = 2.132) showed no significant difference in the certified reference values for the metals and the measured values (at 95% confidence limit) indicating good quality control and data validation. The recovery range of 100.9-135.1% with mean of 118±15 was obtained for the metals, relative to the certified reference values.

3.11.4 Quality Control for BOD Determination

The accuracy of the BOD determination was checked using standard mixture of glucose and glutamic acid. 150 mg each of glucose and glutamic acid (both dried at 103^{o}C for 1hour) was dissolved in 1 litre of distilled water. 1 to 50 dilution water was prepared and the BOD was then determined as described in section 3.4.3b. Theoretically, the BOD should be approximately 220 mg/L.

Table 3.7 gives result of comparison of the theoretical BOD value with those obtained from the quality evaluation. The average value of 235±39 mg/L BOD obtained from the study was comparable (106.8% recovery) to the theoretical value of 220 mg/L BOD, indicating good accuracy.

3.11.5 Quality Control of COD Determination

Accuracy of the COD determinations was validated by determination of the COD of potassium hydrogen phthalate which has a theoretical COD value of 500 mg/L. Potassium hydrogen phthalate, ($HOOCC_6H_4COOK$), was lightly crushed and dried to constant weight at 120^{o}C. 425 mg was dissolved in water and diluted to 1000 mL. COD of this solution was then determined as previously described (section 3.6.3). Table 3.7 gives the results of this quality check. The average value of 494±34 mg/L COD obtained from the control check represented a 98.8% recovery, and a good accuracy.

3.12 APPLICATION OF MODELING TO STUDY OF EFFLUENT QUALITY

3.12.1 Modeling to Estimate Gross Organic Pollution and Eutrophication Potential

The data obtained for physicochemical parameters were subjected to Stepwise Multiple Linear Regression using the SPSS 19.0 software package (Lynwood *et al*., 1990; Sharma and Jain, 2005). The regression was designed to enable the estimation of gross organic pollution level

Table 3.7: Comparison of BOD and COD of standards with experimental values.

Parameters	**Date of Analysis**										**Mean ±S.D**	**Reference Value**
	Nov.' 06	**Jan. '07**	**March '07**	**May '07**	**July '07**	**Sept.' 07**	**Nov' 07**	**Jan' '08**	**March '08**	**May '08**		
BOD mg/L	245	305	255	235	267	190	257	183	195	215	235±39	220
COD mg/L	455	505	560	495	510	485	475	440	502	515	494±34	500

and the eutrophication potential.

The following data were used to run the regression for the estimation of gross organic pollution (as indicated by COD levels): conductivity, Ca, Mg, alkalinity, total hardness, sulphate, phosphate, nitrate, chloride.

Eutrophication potential was estimated by determination of phosphate level, using the model. The data used for this purpose were those of conductivity, Ca, Mg, alkalinity, total hardness, sulphate, phosphate, nitrate, chloride, BOD and COD. The quality of the regression was based on the regression coefficients values.

3.13 STATISTICAL ANALYSES AND CALCULATION OF SPECIAL PARAMETERS.

Varieties of statistical tools were used to process the data obtained in the analysis namely:

- t-test
- analysis of variance
- correlation coefficient
- principal component analysis (PCA)
- graphical biplot
- hierarchical cluster analysis (HCA)
- correspondence analysis (CA).

All statistical treatments mentioned above were performed using Microsoft Excel, SPSS (version19) and Paleontological Statistics Software package for education and data analysis (PAST, version 1.38).

3.13.1: Contamination Factor (CF)

The level of contamination of soil by metals is expressed in terms of a contamination factor (CF) calculated as:

$$CF = \frac{\text{Cm sample}}{(\text{Cm Background})}$$

Where the contamination factor

$CF<1$ refers to low contamination

$1 \leq CF < 3$ means moderate contamination

$3 \leq CF \leq 6$ indicates considerable contamination

$CF>6$ indicates very high contamination

3.13.2: Pollution Load Index (PLI).

Each industrial estate was evaluated for the extent of metal pollution by employing the method based on the pollution load index (PLI) developed by Thomilson *et al.* (1980) as follows

$$PLI = (CF_I \times CF_2 \times CF_3 \times CF_N)^{1/n}$$

Where n is the number of metals studied (six in this study) and CF is the contamination factor calculated in 3.13.1

The PLI provides simple but comparative means for assessing a site quality, where a value of PLI <1 denote perfection

PL1=1 present that only baseline level of pollutants are present

PLI>1 would indicate deterioration of site quality.

3.13.3: Geo-accumulation index (I_{geo}).

Enrichment of metal concentration above baseline concentration was calculated using the method proposed by (Muller, 1969).This assesses the metal pollution in terms of seven (0 to 6) enrichment classes (Appendix 12) ranging from background concentration to very heavily pollute as follows:

$$I_{geo} = \log_2 \frac{\text{Cm Sample}}{1.5 \times \text{Cm Background}}$$

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 GENERAL CHARCTERISTICS OF THE INDUSTRIAL EFFLUENTS

4.1.1. Characteristics of Effluents in Ikeja Industrial Estate

Effluents obtained from Berger Paint, Galvanizing Industries Limited, and Woolen & Synthetic Textile Manufacturing Limited had basic pH while the effluents from the Central Treatment Plant and Hoesch Pipe Mills Ltd. were acidic with low pH values (Tables 4.1a and 4.1b). Mean level of TDS, alkalinity, Ca, Mg, total hardness, SO_4^{2-} and PO_4^{3-}, NO_3^-, BOD, COD were significantly different among the six effluents sampled in Ikeja industrial estate.

The effluents at Ikeja Industrial Estate were coloured and had foul odours which is an indication of high level of dissolved solutes in the effluent. Effluent from Woolen & Synthetic Textile Manufacturing Limited had the highest conductivity (9100±3800 µs/cm) while Hoesch Pipe Mills Ltd. had the lowest conductivity (4700±1500 µs/cm). Woolen & Synthetic Textile Manufacturing Limited is a textile industry that makes use of inorganic compounds as their raw material. This could be the reason why the conductivity was high. The SO_4^{2-}, Cl^- and PO_4^{3-} concentrations were all below the FEPA (1991) standard for all effluent except Berger Paint with SO_4^{2-} value of 577±51 mg/L. The DO levels of all the effluents were below 3.4 mg/L. This is an indication of high load of organic and inorganic compounds in the effluents. The low DO concentration of the effluents may facilitate the release of nutrients in the sediment which results in eutrophication of the water bodies (Sondergaard *et al*., 2003; Jin *et al*., 2006).

The effluents pH range of the central treatment plant (3.3-8.0) and May & Baker (4.1-7.0) were acidic, while Berger Paint, Galvanizing Industries Limited and Woolen & Synthetic Textile Manufacturing limited were basic with values of 6.5-11.0, 7.2-12.8 and 9.2-12.6 respectively. The acidic nature of the central treatment plant (5.6±1.4) and May & Baker

Table 4.1a: Physicochemical characteristics[*] of effluents from Ikeja Industrial Estate.

Site Code		**pH**	**Conductivity**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**Total Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**
KJE-EF	Mean	5.6±1.4	7300±1300	663±190	170±91	23±11	4.3±2.4	49±12	220±40	0.57±0.31	57±56
	Range	3.3-8.0	5000-9000	435-999	36-294	9-47	1.1-9.6	35-78	162-185	0.12-1.04	10-196
KHO-EF	Mean	6.9±0.6	4700±1500	374±110	105±27	19±11	7.1±9.7	82±39	34±24	0.43±0.24	59±64
	Range	5.9-8.0	3000-8000	245-599	38-135	4-47	1.8-25.4	22-146	12-92	0.11-0.83	7-221
KBP-EF	Mean	8.5±1.8	7200±2500	1610±170	216±120	15±10	3.9±3.4	60±33	577±51	0.90±0.31	67±37
	Range	6.5-11.0	4000-12000	1350-1860	65-392	5-37	0.4-9.7	23-104	488-658	0.64-1.06	12-152
KGI-EF	Mean	9.9±1.7	8600±3000	690±310	334±310	11±9	3.1±1.4	57±35	110±48	1.75±0.58	63±35
	Range	7.2-12.8	6000-16000	316-1160	65-1120	3-35	0.6-6.0	15-112	44-187	1.03-2.58	8-143
KWS-EF	Mean	10.6±.1.1	9100±3800	1160±890	316±280	17±13	3.1±2.1	60±32	156±73	0.99±0.29	60±40
	Range	9.2-12.6	4000-16000	604-3600	75-795	4-43	1.3-8.4	21-98	123-363	0.62-1.46	14-152
KMB-EF	Mean	5.5±1.2	6600±2100	838±310	208±55	NA	NA	NA	73±36	0.34±0.22	79±35
	Range	4.1-7.0	5000-12000	455-1470	86-271	NA	NA	NA	33-164	0.15-0.75	29-155

*All units in mg/L except pH with no unit, and conductivity in µS/cm

NA- Not Available

Table 4.1b: Physicochemical characteristics* of effluents from Ikeja Industrial Estate.

Site Code		Cl^-	DO	BOD	COD	Pb	Cd	Zn	Cu	Cr	Ni
KJE-EF	Mean	108±51	1.1±1.5	288±130	473±190	0.04±0.05	0.01±0.01	0.97±0.51	0.049±0.023	0.059±0.025	0.075±0.032
	Range	32-201	0.0-3.6	159-535	298-963	0.006-0.15	0.002-0.029	0.39-1.94	0.019-0.083	0.038-0.128	0.042-0.154
KHO-EF	Mean	60±37	3.4±0.5	157±66	262±96	0.17±0.07	0.011±0.002	0.72±0.24	0.03±0.01	0.15±0.11	0.04±0.02
	Range	24-131	3.0-4.7	65-291	111-382	0.06-0.25	0.007-0.014	0.31-1.05	0.01-0.05	0.03-0.4	0.01-0.08
KBP-EF	Mean	45±14	1.3±1.7	221±130	367±150	0.08±0.12	0.007±0.003	0.69±0.14	0.48±0.08	0.020±0.003	0.04±0.01
	Range	25-69	0.0-4.2	89-559	151-671	0.04-0.44	0.003-0.014	0.46-0.89	0.4-0.67	0.016-0.027	0.001-0.05
KGI-EF	Mean	101±95	1.9±1.8	231±79	399±110	0.05±0.06	0.007±0.003	0.51±0.20	1.06±0.55	0.036±0.027	0.069±0.059
	Range	20-255	0.2-4.0	181-424	281-606	0.006-0.15	0.002-0.014	0.19-0.79	0.15-1.96	0.011-0.08	0.008-0.22
KWS-EF	Mean	65±19	1.8±1.7	209±72	343±130	0.28±0.09	0.009±0.004	0.67±0.29	1.45±0.93	2.54±0.26	0.056±0.041
	Range	38-101	0.2-4.3	130-385	150-617	0.18-0.46	0.003-0.015	0.17-1.24	0.32-3.29	2.0-2.9	0.01-0.15
KMB-EF	Mean	93±57	0.2±0.2	239±93	382±110	0.07±0.04	0.013±0.013	0.67±0.24	0.05±0.02	0.05±0.01	0.05±0.03
	Range	29-187	0.0-0.6	147-451	253-631	0.03-0.15	0.001-0.045	0.18-0.98	0.02-0.08	0.04-0.06	0.01-0.10

*All units in mg/L except pH with no unit, and conductivity in µS/cm

(5.5±1.2) effluents could bring about redox changes in the sediments of the receiving water body, and causes algae bloom in the water body (Ahmad *et al*., 2010). The effluent characteristics were compared with the regulatory limits of the Federal Ministry of Environment (Federal Environmental Protection Agency, 1991) and the World Bank (1995) (Table 4.2) that is based on the assimilative capacity of the receiving water for all categories of industries. The mean BOD and COD of all the effluents as shown in Table 4.1b exceeded the guideline values. This is an indication of high load of gross organic pollutants in the effluents.

The nitrate level of all the effluents exceeded the guideline values of 20 mg/L. The high nitrate level in the effluents will increase growth of algae in the water bodies as a result of eutrophication.

The mean concentrations of the heavy metals, Pb, Cd, Zn, Cu, Cr, and Ni, are all within the FEPA guideline values except Cu in Galvanizing Industries Limited effluent (1.06±0.55 mg/L) and Woolen & Synthetic Textile Manufacturing Ltd (1.45±0.93 mg/L); Cr value in Woolen & Synthetic Textile Manufacturing Ltd effluent was (2.54±0.26 mg/L). The high level of Cu in Galvanizing Industries Limited and Woolen & Synthetic Textile Manufacturing Ltd could be as a result of the nature of raw materials used. Galvanizing Industries Limited is a basic metal type of industry. The Woolen & Synthetic Textile Manufacturing Ltd is a textile industry that makes use of dyes. The mean concentration of Zn in the effluents exceeded the guideline limit for World Bank (1995) while Cr in Hoesch Pipe Mills Ltd effluent exceeded the World Bank limit.

Tables 4.3, 4.4, 4.5, 4.6, 4.7 and 4.8 show the Pearson correlation coefficients amongs pairs of the physicochemical parameters of effluents of Ikeja Industrial Estate. There were significantly positive correlation between DO and SO_4^{2-} (r = 0.664); and DO and Cl^- (r=0.655) for Central Treatment Effluent Plant (Table 4.3), while effluent form Hoesch Pipe Mills Ltd effluent had positive correlation between alkalinity and SO_4^{2-} (r = 0.690); Mg and COD (r = 0.645). Total hardness and Ca (r = 0.714); DO and Mg (r = 0.642) and Total hardness and nitrate (r = 0.725) (Table 4.4). This showed that any condition that affects one will affect the other. Berger Paint effluent showed negative correlation between DO and Mg (r = -0.642) (Table 4.5). Galvanising Industries Limited effluent had strong correlation between Ca and Total hardness (r = 0.753) and nitrate and COD (r = 0.753) (Table 4.6).

Table 4.2: Comparison of physicochemical characteristics[*] of the effluents of Ikeja Industrial Estate with effluent quality standards.

Parameters	This Study						FEPA	World Bank
	KJE-EF	**KHO-EF**	**KBP-EF**	**KGI-EF**	**KWS-EF**	**KMB-EF**	**(1991)**	**(1995)**
pH	**5.6**§	6.9	8.5	**9.9**§	**10.6**§	**5.5**§	6.0 -9.0	6.0 -9.0
Colour	Cloudy	Colourless	Coloured	Colourless	Coloured	Cloudy	NA	NA
Odour	Foul	Foul	foul	Foul	Foul	Foul	NA	NA
Conductivity	7300	4700	7200	8600	9100	6600	NA	NA
TDS	663	374	1610	690	1160	838	2000	NA
Alkalinity	170	105	216	334	316	208	NA	NA
Ca	23	19	15	11	17	ND	200	NA
Mg	4.3	7.1	3.9	3.1	3.1	ND	200	NA
Total hardness	49	82	60	57	60	ND	NA	NA
SO_4^{2-}	220	34	**577**§	110	156	73	500	NA
PO_4^{3-}	0.57	0.43	0.90	1.75	0.99	0.34	5	NA
NO_3^{-}	**57**§	**59**§	**67**§	**63**§	**60**§	**79**§	20	NA
Cl^{-}	108	60	45	101	65	93	600	NA
DO	1.1	3.4	1.3	1.9	1.8	0.2	NA	NA
BOD	**288**§	**157**§	**221**§	**231**§	**209**§	**239**§	30	50
COD	**473**§	**262**§	**367**§	**399**§	**343**§	**382**§	80	250
Pb	0.04	0.17	0.08	0.05	0.28	0.07	<1.0	0.10
Cd	0.01	0.011	0.007	0.007	0.009	0.013	<1.0	0.10
Zn	0.97	0.72	0.69	0.51	0.67	0.67	<1.0	0.50
Cu	0.049	0.03	0.48	**1.06**§	**1.45**§	0.05	<1.0	0.50
Cr	0.059	0.15	0.02	0.036	**2.54**§	0.05	<1.0	0.10
Ni	0.075	0.04	0.04	0.069	0.056	0.05	<1.0	0.50

[*] All units in mg/L except pH with no unit, and conductivity in µS/cm

NA- Not Available

Figures with § are out of the limits

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Table 4.3: Pearson correlation coefficients amongst parameters of effluents at the Central Treatment Plant.

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	0.195	1											
Alkalinity	-0.285	0.389	1										
Ca	0.073	0.134	0.262	1									
Mg	0.185	0.197	0.187	.880[b]	1								
T. Hardness	0.352	0.216	-0.487	0.605	0.624	1							
SO_4^{2-}	0.663[b]	-0.538	0.051	-0.027	-0.187	-0.276	1						
PO_4^{3-}	-0.068	0.477	0.621	-0.29	-0.391	-0.573	-0.314	1					
NO_3^-	0.341	0.139	-0.141	-0.088	0.005	0.083	-0.417	0.165	1				
Cl^-	0.541	0.294	0.035	-0.256	-0.186	-0.153	-.851[b]	0.539	0.242	1			
DO	-.811[b]	0.008	0.357	-0.178	-0.272	-0.382	.664[a]	0.126	-0.133	-.655[a]	1		
BOD	.662[a]	0.102	-0.033	-0.186	-0.023	-0.121	-0.269	-0.022	0.54	0.227	-0.326	1	
COD	0.579	0.29	0.289	-0.177	-0.115	-0.322	-0.265	0.311	0.322	0.35	-0.278	.892[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Table 4.4: Pearson correlation coefficients amongst parameters of Hoesch Pipe Mills effluents.

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	0.26	1											
Alkalinity	0.112	-0.645[a]	1										
Ca	-0.18	-0.398	0.164	1									
Mg	0.29	-0.292	0.274	0.024	1								
T. Hardness	0.18	-0.433	0.321	0.724[a]	0.681[a]	1							
SO_4^{2-}	0.077	0.592	-0.690[a]	-0.716[a]	-0.07	-0.585	1						
PO_4^{3-}	-0.295	-0.247	0.000	0.357	-0.451	-0.086	-0.096	1					
NO_3^-	0.702[a]	0.238	0.131	0.104	-0.253	-0.027	-0.209	-0.034	1				
Cl^-	0.736[a]	0.03	0.271	-0.054	0.693[a]	0.525	-0.193	-0.549	0.342	1			
DO	0.188	0.487	-0.657[a]	-0.566	-0.067	-0.457	0.894[b]	0.127	-0.186	-0.177	1		
BOD	-0.421	0.179	-0.221	-0.525	-0.626	-0.821[b]	0.434	0.307	-0.17	-0.546	0.243	1	
COD	-0.453	0.146	-0.298	-0.489	-0.645[a]	-0.798[b]	0.334	0.222	-0.207	-0.492	0.213	0.920[b]	1

[a] Significant at the 0.05 level.

[b] Significant at the 0.01 level.

Table 4.5: Pearson correlation coefficients amongst parameters of Berger Paint effluents.

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	0.497	1											
Alkalinity	-0.193	0.085	1										
Ca	-0.044	0.63	0.25	1									
Mg	0.920[b]	0.181	-0.274	-0.222	1								
T.Hardness	0.198	0.337	0.202	0.511	-0.005	1							
SO_4^{2-}	-0.275	-0.061	-0.04	0.177	-0.352	0.641[a]	1						
PO_4^{3-}	0.47	0.324	0.553	0.329	0.433	0.372	0.02	1					
NO_3^-	0.393	0.43	-0.165	0.405	0.234	0.725[a]	0.389	0.226	1				
Cl^-	-0.063	0.611	0.435	0.570	-0.291	0.012	-0.365	0.048	0.129	1			
DO	-0.477	0.291	0.068	0.166	-0.642[a]	-0.170	0.182	-0.475	-0.049	0.511	1		
BOD	0.420	-0.010	-0.211	-0.200	0.529	-0.243	-0.620	-0.120	-0.200	-0.131	-0.375	1	
COD	0.155	-0.260	-0.066	-0.139	0.312	-0.087	-0.462	-0.115	-0.192	-0.214	-0.478	0.907[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Table 4.6: Pearson correlation coefficients amongst parameters of Galvanizing Industries Limited effluents.

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T.Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	0.578	1											
Alkalinity	.681[a]	0.358	1										
Ca	-0.385	-0.017	-0.091	1									
Mg	-0.233	-0.221	0.244	.688[a]	1								
T.Hardness	-0.576	-0.368	-0.212	.753[a]	0.567	1							
SO_4^{2-}	-0.009	0.024	-0.238	0.019	0.034	-0.021	1						
PO_4^{3-}	-0.134	0.234	-0.416	0.329	-0.299	0.034	0.182	1					
NO_3^-	0.169	0.279	-0.268	0.438	0.037	0.181	0.199	0.318	1				
Cl^-	0.591	0.015	0.224	-0.052	0.155	-0.079	0.006	-0.323	0.473	1			
DO	-0.403	0.277	-0.400	0.272	-0.364	0.087	-0.258	.642[a]	0.077	-0.600	1		
BOD	0.682[a]	0.246	0.773[b]	-0.415	0.007	-0.264	-0.128	-0.346	-0.437	0.261	-0.552	1	
COD	0.317	-0.141	0.467	-0.552	-0.014	-0.291	-0.020	-0.334	-0.753*	0.019	-0.546	0.840[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Woolen & Synthetic Textile Manufacturing limited effluent had strong positive correlation between conductivity and BOD (r = 0.703); phosphate and nitrate (r = 0.673) (Table 4.7) while May & Baker effluent had correlation between COD and DO (r = 0.653) (Table 4.8).
Analysis of variance (ANOVA) was carried out to check for significant difference among the physicochemical parameters for each of the industries. ANOVA at (p=0.05) showed statistically significant difference in total hardness in Berger Paint effluent, Galvanising Industries Limited and Woolen &Synthetic Textile manufacturing Ltd effluents. SO_4^{2-} and BOD showed statistically significant difference for Hoesch Pipe Mill Ltd effluents and May & Baker effluents respectively while Central Treatment Plant effluent showed no statistically significant difference between the physicochemical parameters.

Analysis of variance (p=0.05) showed statistically significant difference between the effluents studied at Ikeja industrial estate for pH, conductivity, TDS, Ca, Mg total hardness, sulphate, phosphate, DO, Pb, Cu, Cr, and Zn indicating constituents concentrations varied spatially and temporally. Levels of alkalinity, nitrate, chloride, BOD, COD, Cd and Ni showed no significant difference among various sites (effluents).

4.1.2 Characteristics of Effluents in Isolo Industrial Estate

Table 4.9 shows the results of the industrial effluents characteristic of Isolo Industrial Estate. Effluents of Viju Industries (Food &Beverages) were mostly acidic with low pH values of 4.0±0.9. The pH values of Johnson Wax (7.5±1.1 and Afra Chem industries (7.2±1.1) (pharmaceuticals) were within the FEPA (1991) guidelines (6.0-9.0).The conductivity was relatively high as shown on Table 4.9; this may be due to the nature of the raw materials (inorganic based) used in the industries. The TDS alkalinity, calcium, magnesium, TH, SO_4^{2-} and PO_4^{3-} were all within FEPA (1991) guideline limits. The nitrate concentrations was within the FEPA guideline limit for Viju industries with value being 16±3 mg/L, while Johnson Wax and Afra Chem industries had values that exceeded the limit of 20 mg/L.

The low DO concentrations of the effluents from Johnson Wax (2.2±1.2 mg/L); Afra Chem (1.5±0.8 mg/L) and Viju industries (1.9±1.3 mg/L). The low DO values facilitate the release of nutrients in the sediment which results in eutrophication of the water bodies. The mean BOD and COD of all the effluents exceeded the guideline values (Table 4.10). This is an indication of gross organic pollutants loading of the effluents. The mean concentrations of the heavy metals studied were all within the FEPA (1991) guideline limit for the effluents.

Table 4.7: Pearson correlation coefficients amongst parameters of Woolen & Synthetic Textile Manufacturing Limited effluents.

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T.Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	0.577	1											
Alkalinity	-0.404	-0.236	1										
Ca	-0.175	-0.245	0.075	1									
Mg	-0.146	0.059	-0.088	0.492	1								
T.Hardness	-0.037	-0.228	-0.241	0.505	0.121	1							
SO_4^{2-}	0.022	-0.056	-0.290	-0.234	-0.343	-0.338	1						
PO_4^{3-}	0.303	-0.377	-0.147	0.098	-0.194	0.087	0.102	1					
NO_3^-	0.441	-0.202	-0.152	0.334	0.003	0.485	-0.143	0.673[a]	1				
Cl^-	0.519	0.766[b]	-0.291	-0.045	-0.203	0.126	-0.022	0.002	-0.028	1			
DO	-0.176	-0.155	-0.267	0.612	0.010	0.138	0.418	0.204	0.169	0.093	1		
BOD	-0.703[a]	-0.484	0.599	-0.289	-0.232	-0.365	0.150	-0.152	-0.246	-0.630	-0.081	1	
COD	-0.759[a]	-0.283	0.493	-0.171	-0.233	-0.194	0.065	-0.335	-0.314	-0.367	0.104	0.899[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Table 4.8: Pearson correlation coefficients amongst parameters of May & Baker effluents.

	Conductivity	**TDS**	**Alkalinity**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1									
TDS	-0.095	1								
Alkalinity	-0.100	-0.378	1							
SO_4^{2-}	0.006	-0.192	0.205	1						
PO_4^{3-}	0.104	0.123	0.069	-0.026	1					
NO_3^-	-0.353	0.333	0.209	-0.538	-0.144	1				
Cl^-	0.262	-0.138	-0.172	0.490	0.471	-0.398	1			
DO	0.578	0.563	-0.336	-0.309	-0.222	0.068	-0.332	1		
BOD	-0.392	-0.586	0.327	0.119	-0.422	0.352	-0.011	-0.631	1	
COD	-0.341	-0.630	0.400	-0.055	-0.181	0.425	0.068	-0.653[a]	0.925[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Table 4.9a: Physicochemical characteristics[*] of effluents from Isolo Industrial Estate.

Site Code		**pH**	**Conductivity**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**Total Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**
SJW-EF	Mean	7.5±1.1	4900±1400	535±130	204±71	13±15	7.2±7.9	47±41	13±9	0.59±0.49	75±64
	Range	5.7-8.9	3330-7300	323-723	99-313	4-54	1.3-28.6	21-163	5-27	0.16-1.41	18-224
SAF-EF	Mean	7.2±1.1	6500±2600	526±170	288±130	15±15	13.2±14.0	59±47	17±18	1.15±0.74	80±33
	Range	5.7-9.2	2500-10500	341-950	142-500	3-52	1.7-39.4	22-184	1-57	0.10-1.89	5-116
SVJ-EF	Mean	4.0±0.9	4600±1800	477±150	94±35	-**	-	-	172±19	0.57±0.21	16±3
	Range	3.3-5.4	3000-7000	360-731	55-150	NA	NA	NA	149-199	0.22-0.72	13-19

*All units in mg/L except pH with no unit, and conductivity in µS/cm.

** Not Determined

NA- Not Available

Table 4.9b: Physicochemical characteristics* of effluents from Isolo Industrial Estate.

Site Code		Cl^-	DO	BOD	COD	Pb	Cd	Zn	Cu	Cr	Ni
SJW-EF	Mean	48±9	2.2±1.2	92±66	153±97	0.09±0.13	0.026±0.062	0.43±0.14	0.37±1.02	0.02±0.03	0.17±0.47
	Range	33-61	0.4-3.7	22-265	35-391	0.006-0.402	0.00-0.20	0.14-0.57	0.01-3.28	0.00-0.08	0.00-1.50
SAF-EF	Mean	44±12	1.5±0.8	120±53	201±100	0.22±0.44	0.06±0.17	0.39±0.17	0.60±1.2	0.004±0.004	0.03±0.02
	Range	20-60	0.5-2.6	39-189	51-349	0.01-1.43	0.00-0.56	0.17-0.69	0.02-5.41	0.00-0.01	0.01-0.09
SVJ-EF	Mean	50±20	1.9±1.3	147±75	269±140	0.18±0.35	0.002±0.002	0.92±0.16	0.10±0.19	0.003±0.000	0.03±0.04
	Range	26-82	0.0-2.9	62-216	105-385	0.01-0.80	0.000-0.006	0.80-1.18	0.01-0.44	0.003-0.003	0.01-0.11

*All units in mg/L except pH with no unit, and conductivity in µS/cm.

Table 4.10: Comparison of physicochemical characteristics[*] of the effluents of Isolo and Ilupeju Industrial Estates with effluent quality standards.

Parameters	**This Study**					**FEPA (1991)**	**World Bank (1995)**
	SJW-EF	**SAF-EF**	**SVJ-EF**	**LPZ-EF**	**LCA-EF**		
pH	7.5	7.2	4.0§	6	6.5	6.0 -9.0	6.0 -9.0
Colour	Clear	Clear	Cloudy	Cloudy	Coloured	NA	NA
Odour	Odourless	Foul	Foul	Foul	Foul	NA	NA
Conductivity	4900	6500	4600	3117	4065	NA	NA
TDS	535	526	477	385	467	2000	NA
Alkalinity	204	288	94	128	164	NA	NA
Ca	13	15	**	18	21	200	NA
Mg	7.2	13.2	**	5.3	4.5	200	NA
Total hardness	47	59	**	71	69	NA	NA
SO_4^{2-}	13	17	172	10	10	500	NA
PO_4^{3-}	0.59	1.01	0.57	1	0.9	5	NA
NO_3^{-}	**75**§	**80**§	16	**106**§	**137**§	20	NA
Cl^{-}	48	44	50	28	41	600	NA
DO	2.2	1.5	1.9	0.9	0.2	NA	NA
BOD	**92**§	**120**§	**147**§	**136**§	**126**§	30	50
COD	**153**§	**201**§	**269**§	**246**§	**225**§	80	250
Pb	0.09	0.22	0.18	0.02	0.01	<1.0	0.10
Cd	0.026	0.06	0.002	0.04	0.012	<1.0	0.10
Zn	0.43	0.39	0.92	0.25	0.47	<1.0	0.50
Cu	0.37	0.6	0.1	0.22	0.36	<1.0	0.50
Cr	0.02	0.004	0.003	0.006	0.02	<1.0	0.10
Ni	0.17	0.03	0.03	0.04	0.06	<1.0	0.50

*All units in mg/L except pH with no unit, and conductivity in μS/cm^3,

** Not Determined,

NA- Not Available.

Figures with § are out of the limits

Cr concentrations were below the detection limit.

Tables 4.11-4.13 show correlation coefficients between pairs of the physicochemical parameters of effluents at Isolo Industrial Estate. There were high correlations between conductivity vs TDS (r = 0.721); TDS vs. nitrate (r = 0.679); and alkalinity vs. sulphate (r = 0.709) in Johnson Wax effluent (Table 4.11). Afra Chem effluent also showed good correlations between the pairs of TDS and alkalinity (r = 0.710), alkalinity and sulphate (r = 0.632), calcium and magnesium (r=0.700), and sulphate and chloride (r = 0.679) (Table 4.12). Viju Industries effluent had strong correlations for TDS vs. Cl^- (r = 0.906) (Table 4.13).

Analysis of variance (p=0.05) showed significant differences among the sites in Isolo Industrial Estate for the parameters pH, alkalinity, sulphate, nitrate and Zn. Levels of conductivity, TDS, Ca, Mg, TH, phosphate, Cl^-, DO, BOD, COD, Pb, Cd, Cu, Cd, and Ni did not show significant differences among various effluents. Significant differences occurred for pH in John Wax effluent, pH and DO for Afra Chem effluent, while Viju industries effluent showed no significant difference for all the physicochemical parameters.

4.1.3 Characteristics of Effluents in Ilupeju Industrial Estate

Table 4.14a and 4.14b give the characteristics of effluents from Ilupeju Industrial Estate. Effluents of Paterson Zochonis (LPZ-EF) had a pH range of 5.0-7.01 with mean value of 6.0±0.7; the effluents were slightly acidic. The pH range of the canal (LCA-EF) that receives various effluents from the industrial estate was 5.6-7.4 with mean of 6.5±0.6. This slightly acidic pH will support the release of metals from the sediments. The effluents from Paterson Zochonis and the Canal were coloured with foul odours. The Canal was also void of aquatic life.

The conductivities of effluents of Paterson Zochonis and the Canal were (3120±960 µS/cm) and (4070±1400 µS/cm) respectively. Alkalinity, calcium, magnesium, total hardness, sulphate, phosphate and chloride levels differed significantly among the various sampling points of the Paterson Zochonis and Canal effluents.

The DO of effluents at Paterson Zochonis was 0.85±0.70 mg/L and at the Canal 0.20±0.50 mg/L. The low DO value could be responsible for the non-existence of aquatic life in the Canal. Effluents BOD and COD at Paterson Zochonis and the Canal exceeded the guideline values (Table 4.10).

Table 4.11: Pearson correlation coefficients amongst parameters of John Wax Nigeria Ltd. effluents.

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T.Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	0.721[a]	1											
Alkalinity	0.638[a]	0.349	1										
Ca	-0.210	0.033	-0.268	1									
Mg	-0.188	0	-0.236	0.992[b]	1								
T.Hardness	-0.375	-0.076	-0.356	0.971[b]	0.962[b]	1							
SO_4^{2-}	0.643[a]	0.276	0.709[a]	-0.343	-0.293	-0.365	1						
PO_4^{3-}	-0.419	-0.285	-0.278	0.181	0.132	0.169	-0.288	1					
NO_3^-	0.647[a]	0.679[a]	0.163	-0.195	-0.174	-0.326	0.224	-0.156	1	-			
Cl^-	0.166	0.083	0.628	0.199	0.195	0.109	0.183	0.245	0.028	1			
DO	-0.032	0.102	-0.023	-0.575	-0.581	-0.523	-0.239	-0.528	0.22o	-0.208	1		
BOD	-0.005	-0.099	0.537	-0.198	-0.134	-0.118	0.621	-0.179	-0.083	0.266	-0.042	1	
COD	-0.021	-0.057	0.504	-0.219	-0.167	-0.131	0.619	-0.138	-0.059	0.274	-0.024	0.989[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Table 4.12: Pearson correlation coefficients amongst parameters of Afrab chem Ltd effluents.

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T.Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	-0.009	1											
Alkalinity	0.119	0.710^a	1										
Ca	-0.281	-0.178	-0.203	1									
Mg	-0.066	-0.288	0.064	0.700^a	1								
T.Hardness	-0.188	-0.243	-0.205	0.948^b	0.845^b	1							
SO_4^{2-}	-0.017	0.015	0.632^a	0.053	0.510	0.095	1						
PO_4^{3-}	-0.296	-0.232	-0.260	0.277	-0.014	0.205	-0.246	1					
NO_3^-	0.217	0.243	0.233	0.338	0.12	0.205	0.06	0.36	1				
Cl^-	-0.337	-0.407	0.166	0.123	0.386	0.093	0.679^a	-0.090	-0.141	1			
DO	0.863^b	0.245	0.368	-0.344	-0.168	-0.318	0.113	-0.155	0.530	-0.363	1		
BOD	0.208	0.346	0.434	0.305	0.480	0.424	0.067	0.110	0.367	-0.112	0.205	1	
COD	0.140	0.371	0.399	0.258	0.446	0.399	-0.003	0.096	0.294	-0.18	0.151	0.984^b	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Table 4.13: Pearson correlation coefficients amongst parameters of Viju industrieseffluents.

	Conductivity	**TDS**	**Alkalinity**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1									
TDS	0.817	1								
Alkalinity	-0.245	-0.176	1							
SO_4^{2-}	0.388	-0.114	0.214	1						
PO_4^{3-}	0.299	0.469	0.702	-0.057	1					
NO_3^-	0.438	0.535	0.245	0.38	0.232	1				
Cl^-	0.857	0.916[a]	0.122	0.225	0.604	0.711	1			
DO	-0.57	-0.906[a]	0.245	0.509	-0.459	-0.228	-0.69	1		
BOD	0.583	0.255	-0.675	0.522	-0.575	0.319	0.249	0.013	1	
COD	0.519	0.212	-0.699	0.485	-0.635	0.31	0.192	0.041	0.996[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Table 4.14a: Physicochemical characteristics* of effluents from Ilupeju Industrial Estate.

Site Code		**pH**	**Conductivity**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**
LPZ-EF1	Mean	6.1±0.8	3100±1200	453±92	134±81	17±10	5.5±3.4	70±33	9±8	1.1±0.8	144±36
	Range	5.1-7.3	2000-5000	342-630	41-295	5-33	2.3-13,2	37-143	2-29	0.1-2.7	100-301
LPZ-EF2	Mean	5.7±1.3	3860±1200	414±120	136±80	13±8	4.9±3.7	59±35	12±6	1.2±0.9	130±60
	Range	3.4-7.0	2000-5000	274-581	11-236	6-30	1.6-12.2	29-133	4-23	0.1-2.4	10-179
LPZ-EF3	Mean	6.3±0.8	2900±876	295±66	115±49	19±9	5.1±2.9	74±32	13±16	0.6±0.4	54±25
	Range	5.2-7.5	2000-4000	179-401	53-190	8-35	1.4-10.8	43-138	2-54	0.4-1.7	25-91
LPZ-EF	Mean	6.0±0.7	3120±960	385±60	128±56	18±9	5.3±2.9	71±32	10±8	1.0±0.5	106±23
	Range	5.0-7.1	2000-4330	288-472	37-214	6-33	5.3-2.9	38-138	2-26	0.3-1.9	61-137
LCA-EF1	Mean	6.4±0.7	4000±1300	454±140	156±72	21±15	4.5±2.5	71±47	7±3	0.9±0.5	113±52
	Range	5.3-7.5	2000±6000	209-631	70-280	5-56	1.8-9.6	12-189	4-13	0.2-1.5	15-163
LCA-EF2	Mean	6.6±0.8	4130±1400	480±130	173±91	22±10	4.5±2.4	66±29	13±10	1.0±0.7	161±88
	Range	5.9-8.2	2000-6000	270-673	73-357	11-43	1.8--8.7	22-122	4-37	0.2-2.5	10-305
LCA-EF	Mean	6.5±0.6	4070±1400	467±130	164±81	21±13	4.5±1.8	69±38	10±6	0.9±0.5	137±64
	Range	5.6-7.4	2000-6000	275-652	73-319	9-50	2.0--6.5	17-156	4-22	0.2-2.0	13-213

*All units in mg/L except pH with no unit, and conductivity in µS/cm.

Table 4.14b: Physicochemical characteristics[*] of effluent from Ilupeju Industrial Estate contd.

Site Code		**Cl^-**	**DO**	**BOD**	**COD**	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**
LPZ-EF1	Mean	33±27	0.9±1.2	146±130	264±170	0.014±0.018	0.01±0.01	0.16±0.08	0.12±0.18	0.007±0.008	0.05±0.06
	Range	6-87	0.0-3.0	33-462	63-601	0.006-0.064	BDL-0.04	0.03-0.25	0.04-0.63	BDL-0.03	BDL-0.17
LPZ-EF2	Mean	38±23	0.4±0.9	123±160	227±260	0.03±0.01	0.05±0.12	0.32±0.20	0.14±0.08	0.003±0.000	0.07±0.06
	Range	10-76	0.0-2.4	14-470	20-752	0.02-0.05	0.003-0.325	0.03-0.61	0.05-0.26	BDL	0.008-0.139
LPZ-EF3	Mean	18±11	0.8±0.9	138±140	238±230	0.03±0.07	0.08±0.24	0.30±0.14	0.35±0.19	0.01±0.01	0.03±0.03
	Range	8-47	0.0-2.3	35-427	61-726	0.006-0.24	BDL-0.77	0.02-0.59	0.047-0.66	0.003-0.040	BDL
LPZ-EF	Mean	28±18	0.85±0.7	136±119	246±180	0.02±0.03	0.04±0.12	0.25±0.10	0.22±0.10	0.006±0.006	0.04±0.05
	Range	11-65	0.0-1.9	30-453	57-693	0.01-0.12	BDL -0.38	0.03-0.40	0.05-0.35	0.003-0.02	0.01-0.13
LCA-EF1	Mean	38±17	0.3±0.6	141±130	241±210	0.01±0.01	0.01±0.02	0.38±0.44	0.42±0.31	0.01±0.02	0.06±0.12
	Range	10-65	0.0-1.9	36-463	65-741	0.01-0.04	BDL-0.07	0.03-1.28	0.05-0.92	BDL-0.06	0.01-0.39
LCA-EF2	Mean	45±26	0.14±0.3	111±65	210±130	0.02±0.02	0.01±0.02	0.57±0.75	0.31±0.20	0.02±0.06	0.05±0.11

Site Code		Cl$^-$	DO	BOD	COD	Pb	Cd	Zn	Cu	Cr	Ni
	Range	14-81	0.0--1.0	11-197	20-404	0.01-0.08	BDL-0.05	0.03-2.08	0.05-0.59	BDL-0.19	0.01-0.37
LCA-EF	Mean	41±21	0.20±0.5	126±74	225±130	0.01±0.01	0.012±0.017	0.47±0.59	0.36±0.22	0.02±0.04	0.06±0.12
	Range	12-73	0.00-1.4	27-258	51-426	BDL-0.04	BDL-0.05	0.03-1.59	0.05-0.64	BDL-0.13	BDL-0.38

*All units in mg/L except pH with no unit, and conductivity in µS/cm, BDL(Below detection limit = <0.0064 mg/L for Pb, <0.0004 mg/L for Cd, < 0.0031 mg/L for Cr, <0.0082 mg/L for Ni

The nitrate level of the Paterson Zochonis effluents 106±23 mg/L and the Canal 137±64 mg/L all exceeded the FEPA guideline values of 20 mg/L. High nitrate level in the effluents will increase growth of algae in the water bodies. Concentrations of Pb ,Cd ,Zn, Cu, Cr, Ni were within the FEPA (1991) guideline values (Table 4.10). Cd and Cr were below their detection limits.

Table 4.15 and 4.16 give the correlation coefficients between pairs of the physicochemical parameters of effluents studied at the two locations at Ilupeju Industrial Estate. There was positive correlation between conductivity and calcium (r = 0.643), conductivity and nitrate (r = 0.6880); TDS and alkalinity (r = 0.688); while negative correlation exist between conductivity and TH (r = -0.6460) for Paterson Zochonis effluents (Table 4.15). The canal effluents showed good correlation between the following parameters as shown in (Table 4.16), TDS and alkalinity (r = 0.696); TDS and BOD (r = 0.724), TDS and COD (r = 0.7290); calcium and TH (r = 0.738); phosphate and chloride (r = 0.640).

Analysis of variance (p=0.05) showed significant difference among the sites in Ilupeju Industrial Estate for the parameters TDS, nitrate and Cu, indicating constituents concentration variation. Levels of pH, conductivity, alkalinity, Ca, Mg, TH, PO_4^{-}, SO_4^{2-}, Cl^- ,DO, BOD, COD, Pb, Cd, Zn, Cr, and Ni did not show any significant difference. There was no significant difference in Paterson Zochonis and Canal effluents for all the physicochemical parameters analysed.

4.2: CHARACTERISTICS OF EFFLUENTS ACCORDING TO TYPES OF INDUSTRIES

The results of effluent characteristics obtained were examined for patterns related to industry types, i.e pharmaceuticals, textiles, paints, foods and beverages, basic metals, and conglomerates and mixed/collective. For each industry type, results were pooled for all estates.

Pharmaceutical Industry: The parameters of concern in pharmaceutical Industry are TDS, BOD and COD values which may be in the tens of hundreds of milligrams per litre. Effluents of pharmaceutical industries had pH range of 4.1-9.2 with mean of 6.8±1.4 (Table 4.17). The conductivity levels (6000±2200 µS/cm) were much higher than (290 µS/cm) work reported by Adeyeye *et al.*, 2007. The effluents were coloured with foul odour. The TDS, alkalinity, TH, Ca, Mg, SO_4^{2-} , PO_4^{-} and Cl^- levels were within the FEPA (1991) and World Bank (1995) limits. The NO_3^- levels (78±45 mg/L) are not within the FEPA (1991) of 20 mg/L.

Table 4.15: Pearson correlation coefficients amongst parameters of Paterson Zonchouis effluents .

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T.Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	0.457	1											
Alkalinity	0.475	0.688[a]	1										
Ca	-0.643[a]	-0.274	-0.091	1									
Mg	-0.514	-0.63	-0.328	0.785[b]	1								
T. Hardness	-0.646[a]	-0.476	-0.213	0.956[b]	0.903[b]	1							
SO_4^{2-}	0.784[b]	0.191	0.170	-0.589	-0.273	-0.469	1						
PO_4^{3-}	0.598	0.326	0.774[b]	0.044	-0.036	0.011	0.286	1					
NO_3^-	0.688[a]	0.585	0.504	-0.152	-0.228	-0.253	0.508	0.551	1				
Cl^-	0.076	-0.150	0.240	0.092	0.191	0.045	-0.194	0.326	0.327	1			
DO	-0.709[a]	-0.222	-0.458	0.371	0.032	0.322	-0.512	-0.524	-0.528	-0.423	1		
BOD	0.278	0.516	0.134	0.012	-0.206	-0.157	-0.023	-0.016	0.521	0.005	-0.269	1	
COD	0.147	0.491	0.128	0.136	-0.105	-0.041	-0.142	-0.050	0.480	0.049	-0.221	0.986[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level.

Table 4.16: Pearson correlation coefficients amongst parameters of Canal effluents.

	Conductivity	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T.Hardness**	**SO_4^{2-}**	**PO_4^{3-}**	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**
Conductivity	1												
TDS	0.949[b]	1											
Alkalinity	0.627	0.696*	1										
Ca	-0.537	-0.434	0.048	1									
Mg	-0.22	-0.207	-0.584	0.005	1								
T. Hardness	-0.32	-0.173	-0.049	0.738[a]	0.334	1							
SO_4^{2-}	0.21	0.433	0.474	-0.101	-0.447	-0.09	1						
PO_4^{3-}	0.478	0.505	0.775[b]	0.101	-0.439	-0.053	0.308	1					
NO_3^-	-0.303	-0.175	-0.140	0.457	0.057	0.070	0.245	-0.094	1				
Cl^-	0.773[b]	0.780[b]	0.833[b]	-0.064	-0.593	-0.198	0.372	0.646[a]	0.042	1			
DO	0.075	-0.112	0.069	0.002	-0.442	-0.548	-0.35	0.116	0.239	0.358	1		
BOD	-0.600	-0.724[a]	-0.357	0.233	-0.193	-0.081	-0.449	-0.427	-0.015	-0.468	0.393	1	
COD	-0.612	-0.729[a]	-0.384	0.276	-0.111	-0.043	-0.500	-0.467	0.057	-0.477	0.408	0.991[b]	1

[a] Significant at the 0.05 level. [b] Significant at the 0.01 level **

Table 4.17: Physicochemical characteristics* of effluents from different classes of industries.

Effluent types/ Parameters	pH	Conductivity	TDS	Alkalinity	Calcium	Magnesium	Total Hardness	SO_4^{2-}	PO_4^{3-}
Mixed /collective effluent	6.2±1.1	5140±2000	532±180	166±82	22±12	4.4±2.4	63±33	80±100	0.79±0.52
Basic metals	8.4±2.0	6650±3000	532±280	220±240	15±11	5.1±5.2	70±38	71±53	1.09±0.80
Pharmaceuticals	6.8±1.4	6000±2200	633±260	233±97	14±15	10±11	53±44	34±36	0.65±0.57
Paint	8.5±1.8	7200±2500	1610±180	216±120	15±10	3.0±3.4	60±33	577±51	0.90±0.13
Textile	10.6±1.1	9100±3800	1160±890	316±270	17±13	3.1±2.1	40±32	156±73	0.99±0.29
Conglomerate	6.0±0.7	3120±960	385±60	128±56	17.7±9.2	5.3±2.9	71±32	10.3±8.2	0.97±0.49
Food & beverage	4.0±0.9	4600±1800	477±150	94±35	**	**	**	172±19	0.57±0.21
FEPA(1991)	6.0 - 9.0	NA	2000	NA	200	200	NA	500	5
World Bank (1995)	6.0 - 9.0	NA	NA	NA	NA	NA	NA	NA	NA

*All units in mg/L except pH with no unit, and conductivity in μS/cm.

NA – not available;

** not determined,

Table 4.17: Physicochemical characteristics* of effluents from different classes of industries contd.

Effluent types/ Parameters	**NO_3^-**	**Cl^-**	**DO**	**BOD**	**COD**	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**
Mixed /collective effluent	110±78	64±46	0.5±1.0	180±130	308±210	0.034±0.029	0.013±0.016	0.64±0.62	0.26±0.26	0.034±0.040	0.071±0.089
Basic metals	61±50	80±74	2.7±1.5	194±81	330±120	0.11±0.08	0.009±0.004	0.62±0.24	0.55±0.65	0.09±0.10	0.06±0.04
Pharmaceuticals	78±45	61±40	1.3±1.2	150±96	245±140	0.053±0.042	0.012±0.013	0.48±0.20	0.048±0.033	0.030±0.024	0.043±0.021
Paint	67±37	45±14	1.3±1.7	221±130	367±150	0.08±0.12	0.007±0.003	0.69±0.14	0.48±0.08	0.02±0.00	0.04±0.00
Textile	60±32	65±19	1.8±1.7	209±72	343±130	0.28±0.09	0.01±0.00	0.67±0.29	1.45±0.93	2.54±0.26	0.06±0.04
Conglomerate	106±23	28±18	0.85±0.74	136±120	246±180	0.03±0.03	0.04±0.12	0.25±0.10	0.22±0.10	0.01±0.00	0.05±0.04
Food & beverage	15.9±2.5	50±20	1.9±1.3	147±75	269±140	0.04±0.02	0.003±0.002	0.92±0.16	0.02±0.02	0.01±0.00	0.04±0.04
FEPA(1991)	20	600	NA	30	80	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
World Bank (1995)	NA	NA	NA	50	250	0.1	0.1	0.5	0.5	0.1	0.5

*All units in mg/L except pH with no unit, and conductivity in µS/cm,

NA – not available

The DO values were low (1.3±1.2 mg/L). The BOD (150±96 mg/L) and COD (245±140 mg/L) values exceeded the limits of 30 mg/L and 80 mg/L; and 50 mg/L and 250 mg/L for FEPA (1991) and World Bank (1995) respectively (Table 4.17). The release of effluents with high levels of BOD and COD into rivers or stream water will have adverse effects on aquatic life due to depleted oxygen level in water. Similar conclusions were also drawn by Shah (1999) and Khan and Noor (2002). The high levels of BOD and COD could be attributed to the organic nature of the raw materials used in the industry. The TDS and BOD levels were higher than the work reported by (Tariq *et al*., 2006; Bakare *et al*., 2009). Levels of heavy metals (Pb, Cd, Zn, Cu, Cr and Ni) were within the limits of FEPA (1991) and World Bank (1995). However, levels of Pb, Cd, and Cr were lower than the levels reported by (Adeyeye *et al*., 2007 and Tariq *et al*., 2006) but the Cu levels (0.26 mg/L) in this study are higher than (0.15 mg/L and 0.22 mg/L) for the work carried out by (Adeyeye *et al*., 2007 and Tariq *et al*., 2006) respectively. The levels of the metals were lower than similar work carried out on heavy metals concentrations in some pharmaceutical industrial effluents (Anyakora *et al*., 2011; Lokhande *et al*., 2011; Ramola and Singh, 2013)

Textile Industry: The parameters of concern in textile Industry are pH, colour, TDS, BOD, COD and Cr. pH values ranged within 9.2-12.6 with mean being 10.6±1. That is, these effluents were mostly alkaline in nature, and did not meet required guidelines of 6.0-9.0.Similarly, alkaline pH values for textile effluents have been noted by others Rao *et al*., 1993; Aslam *et al*., 2001; Olayinka and Alo, 2004; Mahmood *et al*., 2005; Ahmed, 2007; Rahman *et al*., 2008; Madukasi *et al*., 2013; Ben-Younes *et al*., 2013). The alkaline nature of the effluents was as a result of the use of sodium hydroxide during one of the process of manufacturing textile materials. High pH inhibits the growth of aquatic macrophytes by impairing iron (Fe) and phosphorus uptake (Argo, 2003). The effluents had varied colours which could be attributed to the types of dye used for the production of particular textile. Azo dyes constitute the largest and most diverse group of dyes used. Azo dyes are a group of compounds characterized by the presence of one or more azo bonds (- N = N -) along with one or more aromatic systems. Despite their low toxic effect on receiving bodies, these dyes create an aesthetic problem, colouration of water bodies (Rajamohan and Karthikeyan, 2004) and were found to be the most recalcitrant compounds (Maeir et al., 2004). The conductivity values (9100±3800 µS/cm; 4000-16000 µS/cm) were much higher than levels reported for a textile effluent (3.4-14.5 µS/cm) by Adeyeye and Ayejuyo, 2002 but lower than work done by (Ben-Younes *et al*., 2013). The values of TDS are high (1160±890 mg/L) but still within the standard limits of 2000 mg/L. Similar results were obtained by (Olayinka and Alo, 2004). Alkalinity, TH, Ca, Mg, SO_4^{2-} , $PO_4^{\ 3-}$ and Cl^- were below the FEPA (1991) and World Bank (1995) limits. The DO values were low (1.8±1.7 mg/L), while BOD and COD values exceeded the limits. The DO levels were higher than similar work of (Olayinka and Alo, 2004; Adebayo *et al*., 2007) while the BOD and COD levels are within the values stated by Olayinka and Alo, 2004 but lower than values reported by (Varma and Sharma, 2011; Madukasi *et al*., 2013; Ben-Younes *et al*., 2013). The NO_3^- levels (60±32 mg/L) were not within the FEPA (1991) of 20 mg/L. The results of NO_3^- levels obtained were higher than work done by (Olayinka and Alo, 2004).

Levels of heavy metals (Pb, Cd, Zn and Ni) were within the limits while Cu (1.45±0.93) mg/L and Cr (2.54±0.26 mg/L) values are higher than the FEPA (1991) and World Bank (1995) limits respectively. The high levels of Cu and Cr in textile effluents could be related to the various pigments and additives used in the manufacturing of textile materials.The Cr levels were higher than results stated by (Olayinka and Alo, 2004; Ugoji and Aboaba, 2004; Adebayo *et al*., 2007; Deepali, 2010). The levels of the metals were higher compared to the works done by (Adebayo *et al*., 2007; Younes *et al*., 2013).

Paint Industry: The parameters of concern in paint Industry are pH, TDS, SO_4^{2-} , $PO_4^{\ 3-}$,NO_3^- , BOD ,COD and Cr. pH values were 8.5±1.8 which ranged between 6.5-11.0. The pH was mostly basic; this could be due to the use of ammonia solution as buffer in water based paints. The values of TDS are high (1610±180 mg/L) but still within the standard limits of 2000 mg/L, similar result was obtained in the work done by (Jolly *et al*., 2012). TDS includes inorganic salts such as carbonates, sulphates, chlorides, calcium and magnesium. Alkalinity, TH, Ca, Mg, PO_4^- and Cl^- were within the FEPA (1991) and World Bank (1995) limits. The Cl^- levels are similar to the work carried out by Onuegbu *et al*., 2013 with value 49 mg/L. The SO_4^{2-} (577±51) mg/L and NO_3^- (67±37 mg/L) values are not within the FEPA (1991a) of 500mg/L and 20 mg/L respectively. The SO_4^{2-} and NO_3^- levels were higher compared with Onuegbu *et al*., 2013 work. The DO values were low (1.3±1.7 mg/L), while BOD and COD values exceeded the limits. The BOD and COD values were similar to the results by Onuegbu *et al*., 2013 but the COD values obtained are lower compared with Madukasi *et al*. (2013) and Onuegbu *et al*. (2013) works. The presence of organic compounds such as nitro cellulose used as thickener, alkyd resins and acrylic /styrene co-polymer used as dispersants and binders could be the cause of high content of biodegradable organic matter which impacts the BOD. The availability of oxidizable inorganic compounds such as pigments and additives are responsible for the impact on COD.

The metal values are lower than the standards (Table 4.17) though Zn values were higher than World Bank (1995) standard. The levels of metals obtained were higher compared with the work reported by Jolly *et al*. (2012). Similar work reported by Malakootian *et al*., (2009) ; Lokhande *et al*., (2011); Madukasi, *et al*., (2013) and Onuegbu *et al*., (2013) gave a higher levels of the metals analysed. The discharge of effluents with high levels of Zn to nearby water bodies, though unusual in that it has low toxicity to man, but relatively high toxicity to fish (Oke *et al*., 2006).

Basic Metal Industry: The parameters of concern in Basic Metal Industry are pH, TDS, SO_4^{2-}, NO_3^-, and metals (Zn, Cu, Cr and Ni). pH values ranged within 5.9-12.8 with mean being 8.4±2.0, the effluents were mostly basic. The TDS, alkalinity, TH, Ca, Mg, SO_4^{2-}, PO_4^{3-} and Cl^- levels were within the FEPA (1991) and World Bank (1995) limits, however DO values 2.7±1.5 mg/L were low. The BOD and COD values exceeded the limits. The NO_3^- levels (60±32 mg/L) are not within the FEPA (1991) of 20 mg/L. The values of metals analysed are below the FEPA (1991) limit though Zn and Cu values were higher than World Bank (1995) limits. The levels of Pb, Cd. Cr and Ni were lower than work reported by Sharma and Forster (1994) and Ayenimo *et al*. (2005). The levels of Cu (0.55±0.65 mg/L) are higher compared with values obtained by Sharma and Forster (1994) and Ayenimo *et al*. (2005).

Foods & Beverages Industry: The parameters of concern in Foods & Beverages Industry are pH, TDS, SO_4^{2-} , BOD, COD and Zn. pH values ranged between 3.3-5.4 with mean being 4.0±0.9. The effluents were generally acidic. The observed mean pH of the effluent (4.0±0.9) was much lower than pH 6.0, 8.0 and 8.3 reported for effluents from Nasco, Cadbury Plc in Nigeria (Chukwu, 2008) and Dairy industry (Cristian, 2010). The effluents were acidic and have the potential to acidify the receiving water bodies thereby rendering it unwholesome for aquatic life. Aquatic biota is sensitive to extremes of pH. The effluent may possibly contain weak acids such as CO_2 and hydrated metal ions for instance Al $(H_2O)_6^+$, which contribute to the acidity. The conductivity levels (4600±1800 µS/cm) were much higher than levels reported for a cocoa industry liquid effluent (10 µS/cm) investigated by (Adeyeye *et al.*, 2005). TH, Ca, and Mg were not determined due to the matrix nature of the effluents. SO_4^{2-} , PO_4^{3-}, NO_3^- and Cl^- were below the FEPA (1991) and World Bank (1995) limits. The levels of PO_4^{3-}, NO_3^- and Cl^- were lower while SO_4^{2-} was higher than reported work by (Ipeaiyeda and Onianwa, 2011). The release of detergents used for washing in the factories is a probable source of phosphate in the effluents. Though the phosphate levels are within the limits of 5.0 mg/L, it is nevertheless not too low as to encourage the proliferation of algae growth in the water bodies.The DO values were low (1.9±1.3 mg/L). BOD and COD values were about five times and four times respectively higher than FEPA 1991 limit. The DO range is far below the recommended minimum of 5.0 mg/L for aquatic life and could encourage septic condition in the water bodies. This condition is detrimental to aquatic life. The major pollutant in the effluents from food and beverage industries is organic material which is decomposable by micro-organisms in the water bodies. In breaking down the organic pollutant, the micro-organism consumes the available oxygen in the water. The susceptibility of aquatic life to toxic substance in the effluent is expected to increase when the level of dissolved oxygen is depleted. The effluents BOD levels are far below the BOD level of 1318 mg/L reported for a similar food manufacturing and beverage industries in Ghana (Acquah, 1998).

Pb, Cd, Cu, Cr and Ni values were below the limits. However, Zn levels were about two times higher than the World Bank limit. The release of effluents with high level of Zn into water bodies will have effect on the aquatic life. The levels of the metals were lower than the reported works of (Amuda *et al.*, 2006; Ipeaiyeda and Onianwa, 2011; Vanerkar *et al.*, 2013).

Conglomerate Industry: pH values ranged within 5.0-7.1 with mean being 6.0±0.7. The pH values are slightly acidic. The acidic nature of the effluent could be attributed to the nature of the raw material used for the manufacturing of the various products which includes range of soaps, cosmetic products, pharmaceutical, etc. The pH values are similar to work done by Ajibola and Ladipo (2009). The conductivity levels (3120±960 µS/cm) were almost the same for a similar work reported with value 3320 µS/cm by Sanyaolu *et al.* (2013). The high values obtained in this work are similar to the result obtained by Nwaedozie (2006). The parameter of concern can make receiving water bodies unsuitable for direct domestic use. This can be said that high conductivity gives an indication of dissolved ions in the effluent samples, hence gives high total dissolved solid which is potentially unhealthy.The total hardness, Ca, Mg, SO_4^{2-} , $PO_4^{\ 3-}$, NO_3^- and Cl^- were below the FEPA (1991) and World Bank (1995) limits. NO_3^- values were five times higher than FEPA limit of 20 mg/L, also greater than nitrate levels reported by Ajibola and Ladipo (2009) and Sanyaolu *et al*. (2013). The levels of SO_4^{2-}, PO_4^{3-} and Cl^- were lower than work reported Ajibola and Ladipo (2009) and Sanyaolu *et al*. (2013). The DO values 0.85±0.74 mg/L are low, which suggested that the industry was releasing some organic substances that were high oxygen-demanding wastes (Emongor *et al*., 2005), thus cannot support aquatic life. The BOD values are five times and three times higher than FEPA (1991) and World Bank (1995) limits respectively while COD values are three times higher than FEPA limit. The DO, BOD and COD levels were lower than work reported by Ajibola and Ladipo (2009). Pb, Cd, Zn, Cu, Cr and Ni values were below the FEPA (1999) and World Bank (1991) limits. The levels of metals were lower compared to the works done by Ajibola and Ladipo (2009) and Sanyaolu *et al*. (2013). However, continues discharge of effluent with low level of metal will pose a great danger to the receiving water bodies, its inhabitants (fishes and other aquatic organisms) as well as those who make use of the water for direct domestic purposes.

Mixed/ Collective Effluent Type: pH values ranged from 3.3-8.0 with a mean of 6.2±1.1. The pH was mostly acidic. TH, Ca, Mg, SO_4^{2-} , PO_4^- and Cl^- were below the FEPA (1991) and World Bank (1995) limits. NO_3^- values are six times higher than FEPA limit of 20 mg/L. The mixed effluents had the least value of DO (0.5±1.0) mg/L compared to other types of industries. The BOD values were six times and four times higher than FEPA (1991) and World Bank (1995) respectively. COD values were four times higher than FEPA (1991) limit. Pb, Cd, Cu, Cr and Ni values are low than the FEPA (1991) limit, however Zn values are higher than the World Bank (1995) limit.

Analysis of variance ($p=0.05$) shows significant difference among the types of industries for pH, conductivity, TDS, alkalinity, Ca, total hardness, sulphate, nitrate, dissolved oxygen, Pb, Cd, Zn, Cu, Cr and Ni indicating constituent concentration varied spatially and temporally. Levels of Mg, phosphate, chloride, biochemical oxygen demand and chemical oxygen demand did not show significant difference among the types of industries.

4.2.1: Multivariate Analysis for Heavy Metals in Types of Industry.

Principal Component Analysis (PCA) was used to categorize the various types of industries according to the similarities in the heavy metal levels. PCA of heavy metal for seven effluents types indicated that the first two components (PC1 and PC2) accounted for 97.3% of the total variation (Table 4.18). A plot of the first two components showed four different groups characterized by their metal concentrations. Cluster 1 was characterized by food & beverages types of effluent with the highest Zn concentrations, cluster 2 by pharmaceuticals, collective and conglomerate types of effluents with least metal (Pb, Cd, Cu, Cr and Ni) concentrations, cluster 3 by Paint and Basic metal types of effluents with highest Ni and Cd concentrations and finally cluster 4 with Textile type of effluents with the highest metal (Pb, Cu and Cr) concentrations. From the PCA biplot (Fig 4.1), Textile types of effluents stand to contribute Pb, Cu and Cr to the environmental media. Cluster formed by the PCA were confirmed by the cluster analysis dendrogram in Figure 4.2, where four different clusters were noticed. Cluster 1 dominated by food & beverages types of effluent, cluster 2 by pharmaceuticals, collective and conglomerate types of effluents having similar metal concentrations, cluster 3 by paint and basic metal effluents having very similar metal concentrations and finally cluster 4 with textile effluents.

Generally, textile effluents have the highest load of the metal studied while the foods & beverage effluent had the least concentrations of the metal studied except Zn concentrations. The order of the metal concentrations in the types of effluents studied is textile > paint and basic metal > pharmaceuticals, collective and conglomerate > foods & beverages.

4.3 EFFECT OF SEASONAL VARIATION ON THE EFFLUENTS CHARACTERISTICS

Table 4.19, 4.20 and 4.21 show the seasonal average concentrations of effluent quality parameters from Ikeja, Isolo and Ilupeju industrial estate respectively.

4.3.1 pH and Alkalinity

pH values indicated no seasonal trend (Figure 4.3). The alkalinity was generally higher in the dry seasons compared to the wet seasons for most of the sites (Table 4.19, 4.20 and 4.21). The high alkalinity could be as a result of detergents and soap based products or raw materials like calcium carbonate that are used in these industries. High alkalinity effluents discharged in water bodies will neutralize acidic pollution from rainfall or basic inputs thereby maintaining the buffering capacity of a water body. Figure 4.4 shows the monthly trends in alkalinity.

Table 4.18: Principal component analysis of data of industrial effluent metal concentrations.

	Eigen Values	Percentage variance	Cumulative percentage
PC 1	2.68724	77.963	77.963
PC 2	0.66571	19.314	97.28
PC 3	0.070936	2.058	99.3 4
PC 4	0.021465	0.62276	99.96
PC 5	0.001084	0.031457	99.99
PC 6	0.000378	0.010972	100

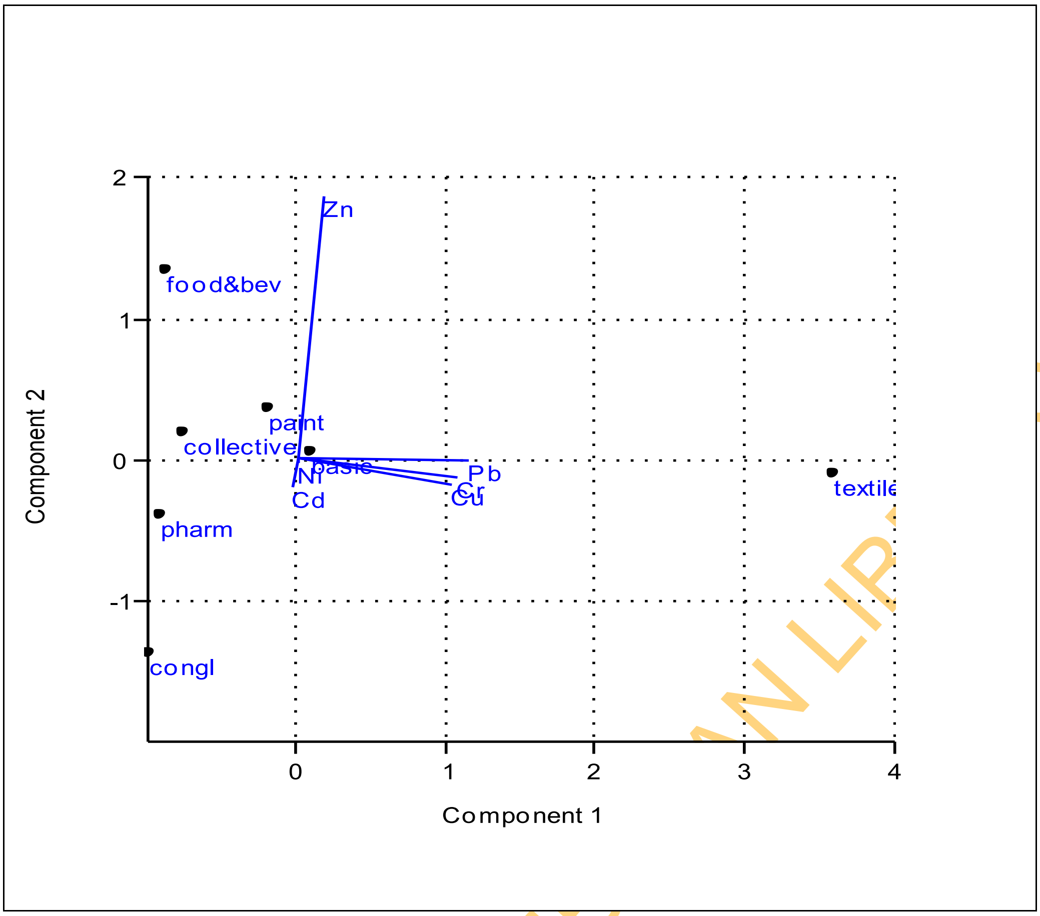

Fig 4.1: Principal component biplot of data on effluents metals concentrations.

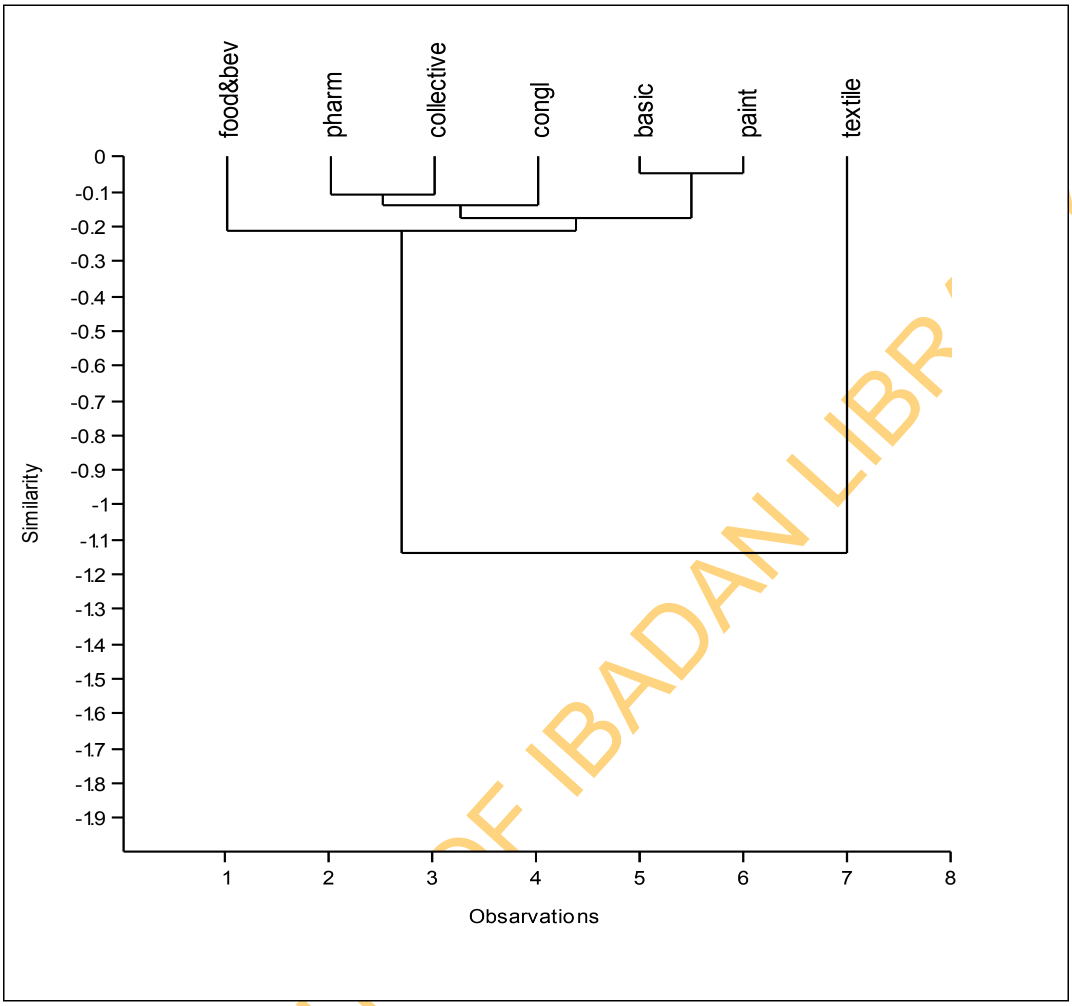

Fig. 4.2: Cluster analysis dendrogram of effluents types for six metal concentrations.

Table 4.19a: Average seasonal effluent quality* at Ikeja Industrial Estate.

Site Code	**Wet Season**							**Dry Season**						
	pH	**Cond**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardness**	**pH**	**Cond**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardness**
KJE-EF	5.7±1.8	7830±1200	749±200	157±110	22±14	4.6±2.7	52±15	5.4±0.8	6500±1300	534±100	190±55	25±5	3.8±2.1	45±5
KHO-EF	6.9±0.6	4670±1750	355±95	110±18	23±12	5.9±1.8	91±28	6.9±0.8	4750±1300	402±140	98±40	12±7	8.9±11.0	68±52
KBP-EF	8.5±1.7	7500±2300	1670±200	254±100	17±11	3.7±3.2	79±30	8.6±2.1	6750±3100	1529±120	158±120	11±7	4.1±4.1	32±9
KGA-EF	9.5±1.6	7500±1600	536±200	250±130	15±10	3.5±1.4	80±25	10.5±2.0	10300±4000	921±330	461±480	6±4	2.6±1.3	24±9
KWS-EF	10.6±1.0	9330±4700	1330±1100	269±250	21±15	3.7±2.4	78±25	10.7±1.4	8750±2600	903±350	385±340	11±8	2.0±0.8	33±21
KMB-EF	5.8±1.3	6830±2600	938±350	195±61	**	**	**	5.1±1.1	6250±1300	689±190	227±45	**	**	**

*All units in mg/L except pH with no unit, and conductivity in µS/cm

** not determined

Table 4.19a contd.:

Site Code	**Wet Season**							**Dry Season**						
	SO_4^{2-}	**PO_4^{3-}**	**NO^{3-}**	**Cl^-**	**DO**	**BOD**	**COD**	**SO_4^{2-}**	**PO_4^{3-}**	**NO^{3-}**	**Cl^-**	**DO**	**BOD**	**COD**
KJE-EF	197±27	0.6±0.4	75±67	126±47	0.7±1.4	315±160	495±250	255±27	0.5±0.2	29±15	81±51	1.7±1.7	248±26	439±66
KHO-EF	22±10	0.4±0.2	66±78	59±32	3.2±0.3	137±40	246±85	51±29	0.5±0.3	49±41	61±50	3.7±0.7	187±93	285±120
KBP-EF	596±45	1.0±0.1	85±36	46±18	1.3±2.0	186±64	336±140	546±49	0.8±0.1	40±22	44±5	1.2±1.3	273±101	414±170
KGA-EF	111±39	1.7±0.6	68±45	118±105	1.9±1.7	214±54	383±130	108±66	1.8±0.7	56±15	76±87	2.1±2.2	256±110	424±92
KWS-EF	135±11	1.0±0.4	69±50	72±20	1.8±1.8	182±42	315±100	188±120	1.0±0.2	46±16	55±11	1.8±1.7	251±95	385±69
KMB-EF	63±19	0.4±0.2	79±20	83±53	0.3±2.0	190±51	340±86	89±52	0.3±0.3	78±54	107±68	0.0±0.0	312±100	444±120

*All units in mg/L except pH with no unit, and conductivity in µS/cm

Table 4.19b: Seasonal concentrations (mg/L) of heavy metals in effluent at Ikeja Industrial Estate.

Site Code	**Wet Season**						**Dry Season**					
	Pb	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**
KJE-EF	0.04±0.04	0.01±0.01	1.15±0.56	0.04±0.03	0.06±0.03	0.08±0.04	0.05±0.07	0.01±0.01	0.70±0.32	0.07±0.01	0.05±0.01	0.07±0.01
KHO-EF	0.17±0.08	0.01±0.00	0.76±0.28	0.03±0.01	0.12±0.08	0.05±0.02	0.17±0.07	0.01±0.00	0.67±0.20	0.03±0.01	0.21±0.13	0.03±0.02
KBP-EF	0.11±0.16	0.008±0.004	0.75±0.15	0.51±0.08	0.022±0.004	0.04±0.01	0.045±0.005	0.006±0.002	0.61±0.09	0.44±0.04	0.019±0.002	0.041±0.007
KGI-EF	0.03±0.04	0.006±0.004	0.50±0.21	1.10±0.46	0.03±0.03	0.05±0.02	0.07±0.08	0.008±0.001	0.53±0.23	1.00±0.74	0.04±0.03	0.10±0.09
KWS-EF	0.32±0.09	0.009±0.004	0.58±0.27	1.20±0.87	2.46±0.27	0.05±0.05	0.23±0.05	0.010±0.003	0.79±0.30	1.83±1.01	2.66±0.21	0.06±0.02
KMB-EF	0.05±0.03	0.018±0.014	0.58±0.24	0.05±0.02	0.05±0.01	0.04±0.02	0.08±0.05	0.005±0.004	0.68±0.25	0.04±0.02	0.05±0.01	0.07±0.04

Table 4.20a: Average seasonal effluent quality* at Isolo Industrial Estate.

Site Code	**Wet Season**							**Dry Season**						
	pH	**Conductivity**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardness**	**pH**	**Conductivity**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardness**
SJW-EF	6.9±1.0	4720±1200	507±137	194±78	18±18	10.0±9.3	59±51	8.4±0.6	5165±1731	575±130	219±69	6±2	3.0±1.4	29±7
SAF-EF	6.5±0.7	5170±2200	491±77	268±120	18±18	17.9±16.0	71±58	8.3±0.6	8500±1600	577±260	317±160	11±10	6.1±5.1	41±18
SVJ-EF	4.4±1.0	5670±1500	548±160	89±6	**	**	**	3.4±0.1	3000±0	370±14	103±67	**	**	**

*All units in mg/L except pH with no unit, and conductivity in µS/cm

** not determined

Table 4.20a contd.:

Site Code	Wet Season							Dry Season						
	SO_4^{2-}	PO_4^{3-}	NO_3^-	Cl^-	DO	BOD	COD	SO_4^{2-}	PO_4^{3-}	NO_3^-	Cl^-	DO	BOD	COD
SJW-EF	11±8	0.5±0.5	60±81	47±8	2.0±1.3	89±88	144±130	17±11	0.7±0.5	96±21	49±11	2.4±1.1	96±16	167±41
SAF-EF	16±20	1.1±0.8	64±34	49±9	1.0±0.5	116±62	200±120	18±18	1.2±0.8	103±11	38±14	2.3±0.5	126±44	203±97
SVJ-EF	173±25	0.6±0.1	16±3	59±21	1.3±1.5	158±84	281±150	170±10	0.5±0.4	16±2	37±14	2.8±0.2	131±86	250±170

*All units in mg/L except pH with no unit, and conductivity in µS/cm

Table 4.20b: Seasonal concentrations (mg/L) of heavy metals in effluent at Isolo Industrial Estate.

Site Code	**Wet Season**						**Dry Season**					
	Pb	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**
SJW-EF	0.**06**±0.11	0.006±0.007	0.44±0.11	0.06±0.03	0.03±0.03	0.02±0.01	0.14±0.18	0.06±0.10	0.40±0.19	0.8±1.6	0.006±0.006	0.40±0.73
SAF-EF	0.055±0.07	0.006±0.006	0.42±0.15	0.07±0.06	0.005±0.005	0.02±0.02	0.48±0.67	0.14±0.28	0.35±0.21	1.39±2.68	0.003±0.000	0.032±0.036
SVJ-EF	0.018±0.019	0.002±0.003	0.94±0.21	0.16±0.24	0.003±0.000	0.04±0.06	0.42±0.53	0.0004±0.000	0.89±0.13	0.01±0.00	0.003±0.000	0.013±0.001

Table 4.21a: Average seasonal of effluent quality* at Ilupeju Industrial Estate.

Site Code	Wet Season							Dry Season						
	pH	**Conductivity**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardess**	**pH**	**Conductivity**	**TDS**	**Alkalinity**	**Ca**	**Mg**	**T. Hardess**
LPZ-EF1	6.0±0.9	2830±1200	440±110	116±77	16±11	5.4±4.0	71±39	6.1±0.9	3500±1300	473±73	162±91	18±11	5.7±2.9	69±29
LPZ-EF2	5.4±1.4	3600±1300	381±120	108±76	16±9	6.1±3.8	68±38	6.4±0.8	4500±710	495±122	206±42	7±1	1.9±0.4	36±10
LPZ-EF3	6.3±0.8	2830±750	281±67	97±48	18±11	6.1±3.1	77±37	6.4±1.0	3000±1200	317±68	142±43	20±6	3.5±1.8	69±26
L PZ-EF	5.9±0.8	3000±840	370±64	109±58	17±10	5.8±3.3	73±36	6.2±0.6	3290±1200	409±54	409±54	18±10	4.5±2.2	67±29
LCA-EF1	6.4±0.8	4330±1400	477±150	170±85	23±19	4.3±2.9	86±58	6.2±0.8	3500±1300	419±130	134±50	18±6	4.9±2.1	52±13
LCA-EF2	6.8±0.9	4500±1500	519±120	197±110	25±13	4.9±2.7	74±35	6.4±0.6	3580±1200	421±150	136±57	17±4	3.8±2.0	53±11
LCA-EF	6.6±0.6	4420±1400	498±130	183±95	24±16	4.6±2.0	80±46	6.3±0.7	3540±1200	420±140	135±54	15±6	4.4±1.7	53±12

*All units in mg/L except pH with no unit, and conductivity in µS/cm

Table 4.21a contd.:

Site Code	Wet Season							Dry Season						
	SO_4^{2-}	PO_4^{3-}	NO_3^-	Cl^-	DO	BOD	COD	SO_4^{2-}	PO_4^{3-}	NO_3^-	Cl^-	DO	BOD	COD
LPZ-EF1	8±5	1.1±1.0	125±21	30±24	0.7±1.0	101±57	203±120	11±12	1.2±0.6	171±39	38±34	1.3±1.4	213±180	357±210
LPZ-EF2	9±4	0.9±1.0	111±62	39±27	0.6±1.0	75±52	163±120	20±4	2.0±0.1	177±3	34±9	0.0±0.0	242±320	386±520
LPZ-EF3	14±20	0.7±0.5	71±14	19±14	1.0±1.1	135±120	234±180	10±11	0.5±0.1	28±2	15±3	0.6±0.4	141±190	244±320
L PZ-EF	10±7	0.9±0.6	102±23	30±21	0.8±0.8	108±44	208±90	11±11	1.0±0.4	111±27	29±16	0.9±0.8	177±188	303±270
LCA-EF1	7±3	1.1±0.5	127±56	43±15	0.3±0.8	100±65	174±110	8±3	0.5±0.2	92±46	30±20	0.2±0.2	201±190	340±290
LCA-EF2	11±7	1.2±0.7	152±81	51±27	0.2±0.4	121±58	231±130	16±14	0.6±0.4	175±110	36±23	0.1±0.2	96±81	178±150
LCA-EF	9±4	1.2±0.5	139±65	47±21	0.2±0.6	111±54	202±110	12±7	0.5±0.2	133±73	33±22	0.1±0.2	148±100	260±170

*All units in mg/L except pH with no unit, and conductivity in µS/cm

Table 4.21b: Seasonal concentrations (mg/L) of heavy metals in effluent at Ilupeju Industrial Estate.

Site Code	Wet Season						Dry Season					
	Pb	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**
LPZ-EF1	0.02±0.02	0.01±0.01	0.13±0.19	0.16±0.23	0.003±0.000	0.06±0.06	0.01±0.00	0.003±0.005	0.19±0.03	0.07±0.02	0.01±0.01	0.05±0.08
LPZ-EF2	0.03±0.01	0.07±0.14	0.28±0.17	0.16±0.09	0.003±0.000	0.06±0.06	0.02±0.00	0.008±0.001	0.40±0.30	0.10±0.01	0.003±0.000	0.09±0.06
LPZ-EF3	0.05±0.10	0.13±0.31	0.30±0.18	0.32±0.22	0.003±0.000	0.03±0.03	0.01±0.00	0.002±0.002	0.3±0.1	0.4±0.2	0.01±0.02	0.02±0.02
L PZ-EF	0.03±0.04	0.06±0.15	0.23±0.11	0.21±0.11	0.003±0.000	0.05±0.050	0.01±0.00	0.004±0.003	0.27±0.09	0.22±0.08	0.01±0.01	0.04±0.05
LCA-EF1	0.01±0.01	0.02±0.03	0.32±0.40	0.39±0.35	0.01±0.02	0.09±0.15	0.01±0.00	0.007±0.006	0.46±0.55	0.46±0.29	0.003±0.000	0.02±0.02
LCA-EF2	0.02±0.03	0.01±0.02	0.56±0.79	0.34±0.20	0.03±0.08	0.07±0.15	0.01±0.00	0.013±0.02	0.57±0.81	0.26±0.24	0.005±0.004	0.014±0.011
LCA-EF	0.02±0.02	0.014±0.020	0.44±0.59	0.36±0.23	0.02±0.05	0.08±0.15	0.01±0.00	0.01±0.01	0.51±0.68	0.36±0.24	0.004±0.002	0.018±0.011

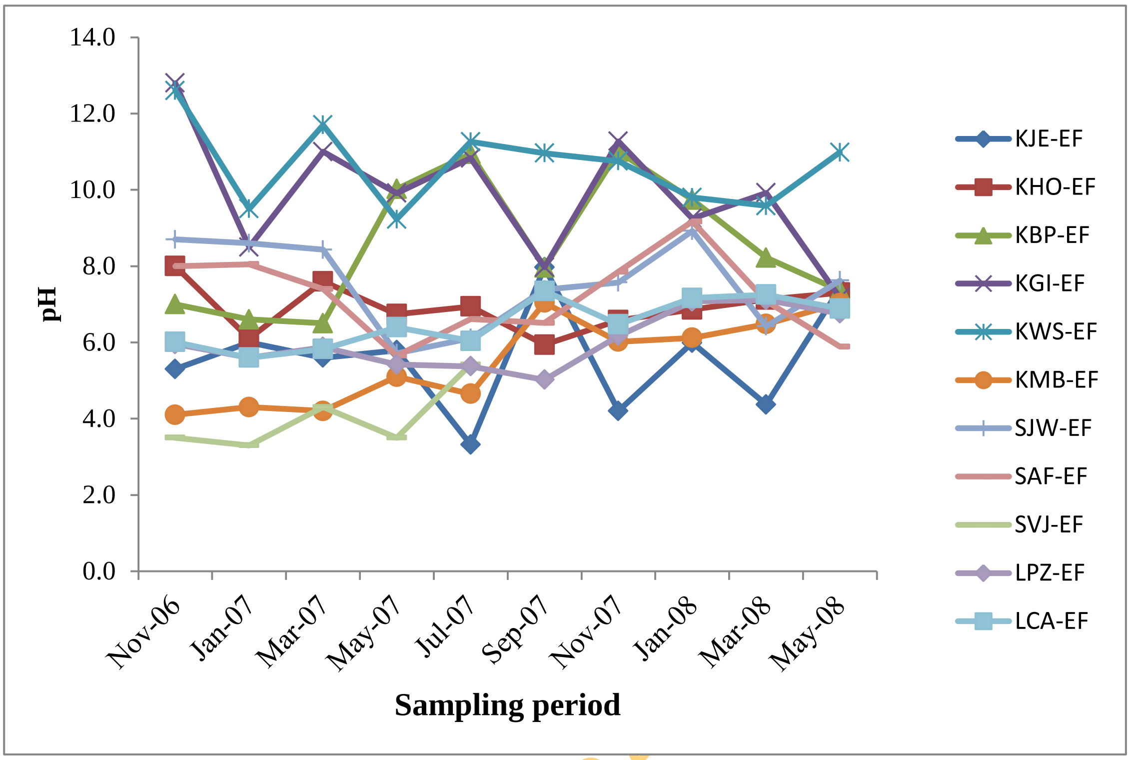

Fig. 4.3: Variations of pH of effluents with sampling period.

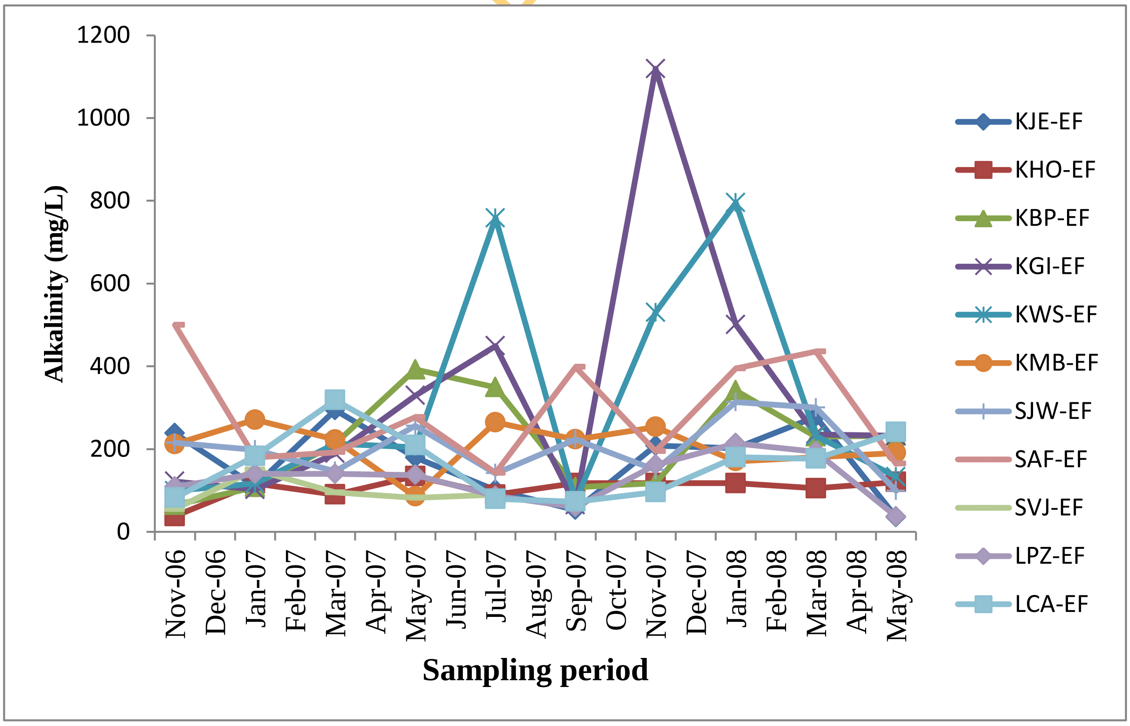

Fig. 4.4: Variations of alkalinity of effluents with sampling period.

The acidic nature of the industrial effluents of the central effluent treatment plant, May & Baker and Viju industries Ltd reflected on the low average alkalinity levels compared to effluents of Berger Paint, Galvanizing Industries Limited and Woolen and Synthetic Textile Manufacturing Limited that are basic. The alkalinity of the basic effluents is quite higher compared to the acidic effluents. The highest alkalinity levels were obtained during the months of Nov. 2007 and Jan. 2008 (the dry seasons) for Galvanizing Industries Limited and Woolen and Synthetic Textile Manufacturing Limited effluents

4.3.2 Total Dissolved Solids (TDS) and Conductivity

Figure 4.5 and 4.6 give the monthly trends in TDS and conductivity respectively. The TDS level and conductivity are higher in the wet season than the dry season for most of the effluents. High values of EC shows that inorganic ions such as H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO^- - e.t.c. are present in reasonable concentrations in the wastewater; Such ions have major influence on the conductivity of water. For TDS, high values obtained indicate that reasonable amount of solid matter were present in the wastewater as dissolved substances. (Uwidia and Ukulu, 2013).Basic effluents had higher TDS and conductivity compared to acidic effluents, this could be associated to the formation of hydroxide ions of various inorganic components of the effluents. The highest conductivity was observed in the month of September, 2007 which corresponded to end of the wet season.

4.3.3 Total hardness, Calcium and Magnesium

Figures 4.7 to 4.9 show the monthly trends in total hardness, calcium and magnesium contents of the effluents. The levels were higher in the wet season than the dry season for most of the effluents. The highest values of TH, calcium and magnesium were observed in the month of July, 2007 for most of the effluents. There was no seasonal trend for the parameters for all the effluents. Analysis of variance ($p = 0.05$) showed significant difference in levels of total hardness, calcium and magnesium among effluents.

4.3.4 Sulphate and Chloride

Figures 4.10 and 4.11 show the monthly trends in sulphate and chloride of the effluents. The sulphate levels are higher in the dry season compared to the wet season for most of the

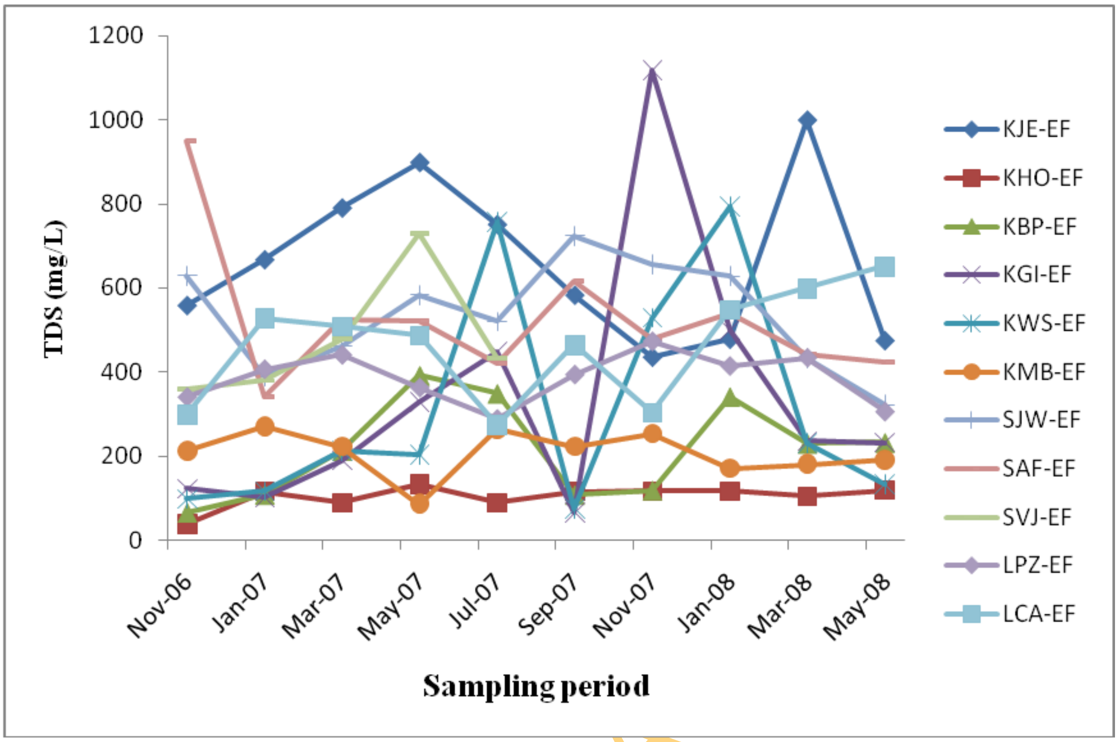

Fig. 4.5: Variations of TDS of effluents with sampling period.

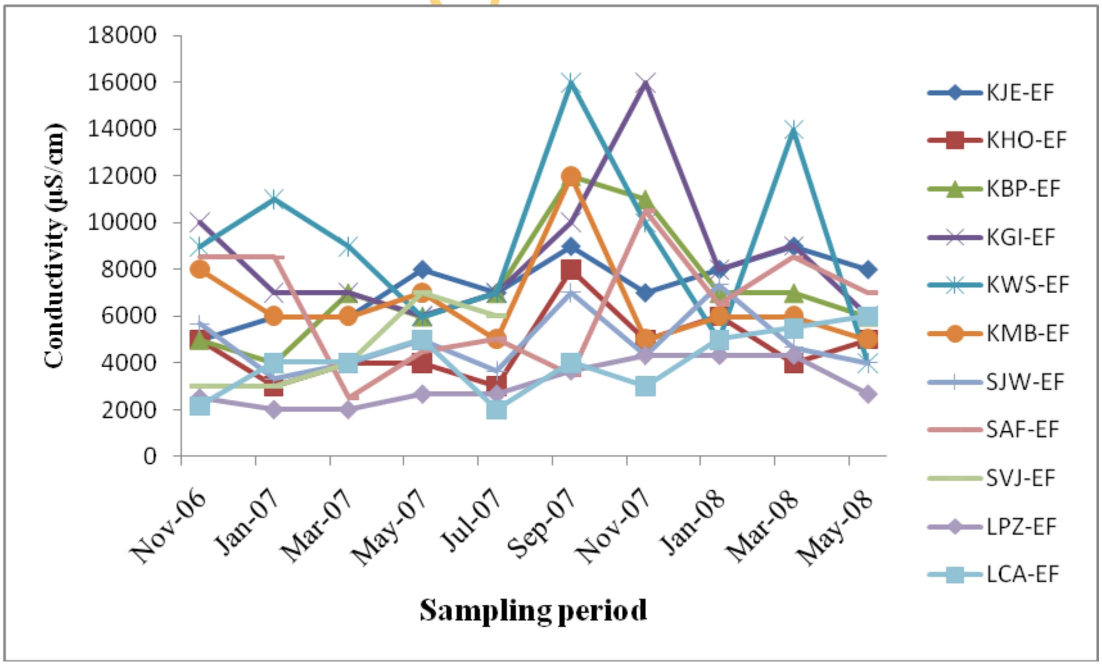

Fig. 4.6: Variations of conductivity of effluents with sampling period.

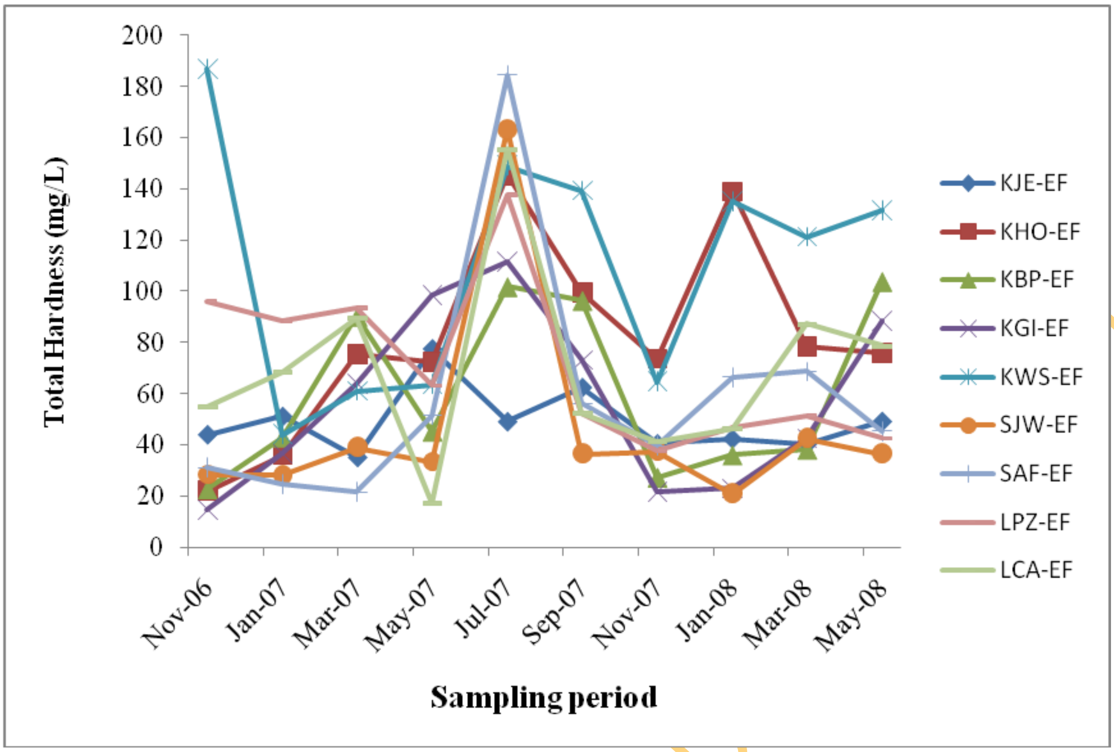

Fig. 4.7: Variations of total hardness of effluents with sampling period.

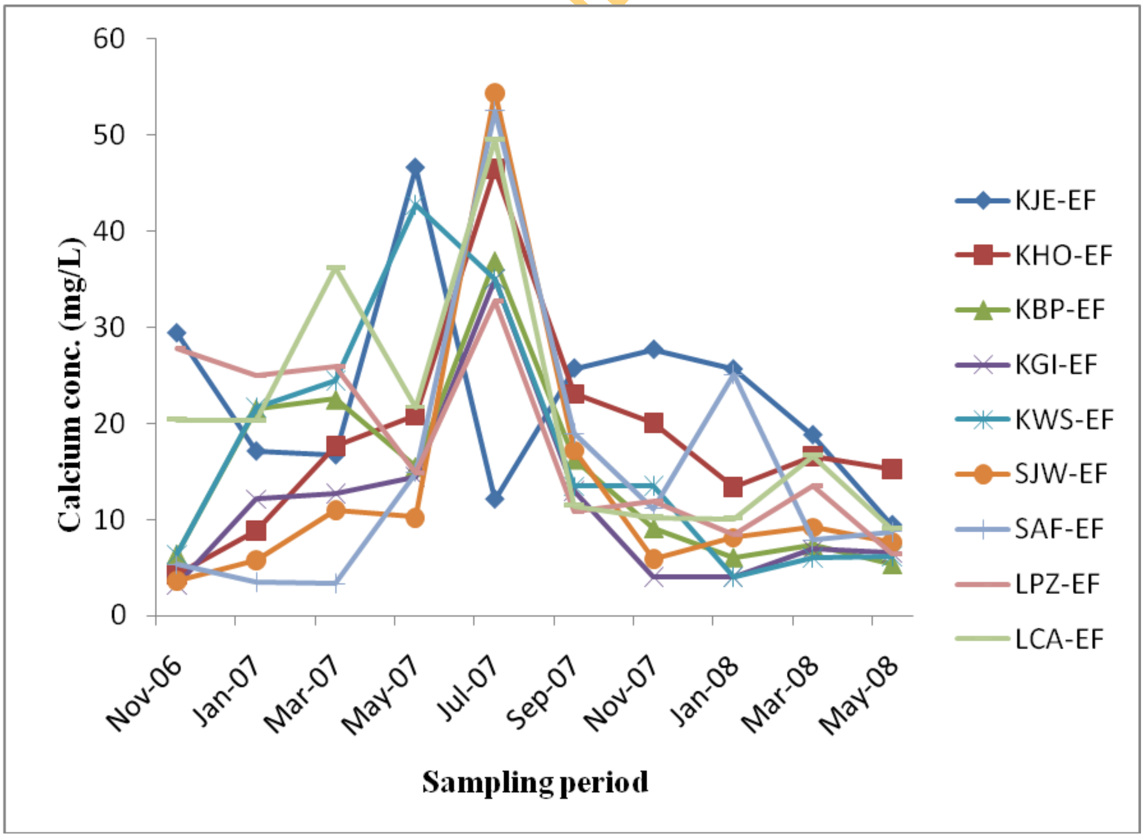

Fig. 4.8: Variations of calcium contents of effluents with sampling period.

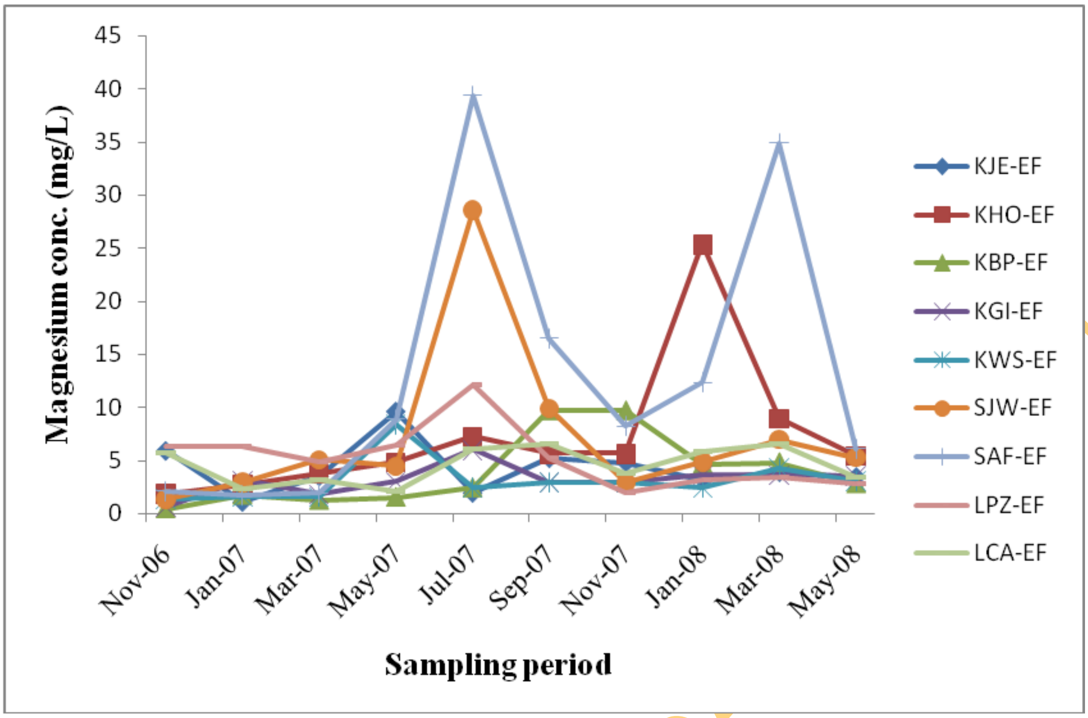

Fig. 4.9: Variations of magnesium contents of effluents with sampling period.

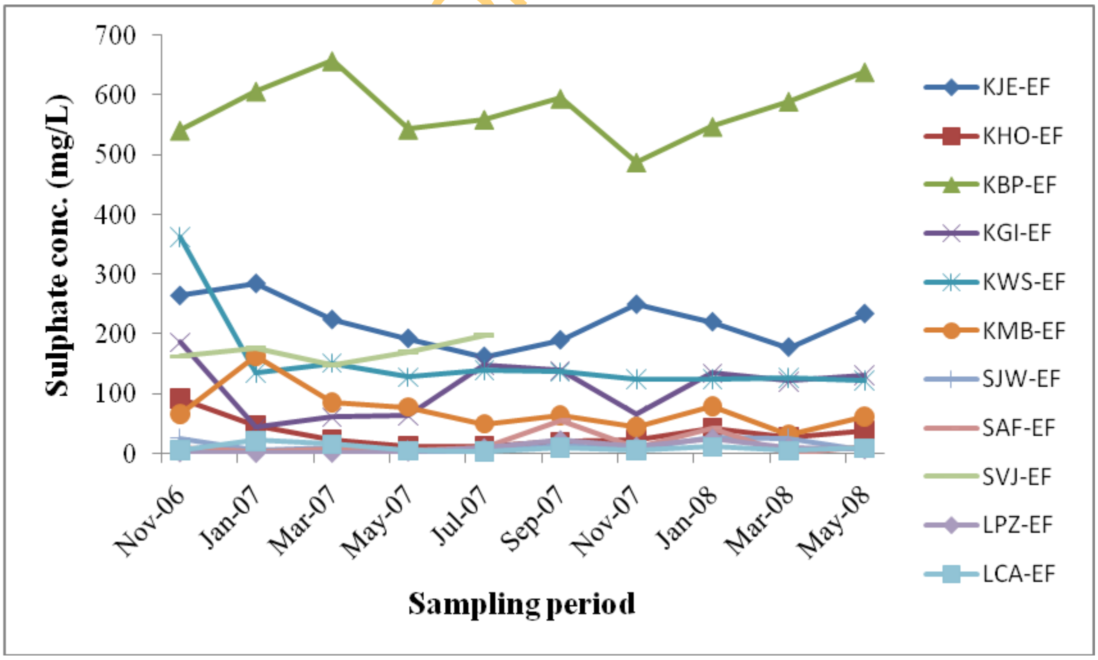

Fig. 4.10: Variations of sulphate contents of effluent with sampling period.

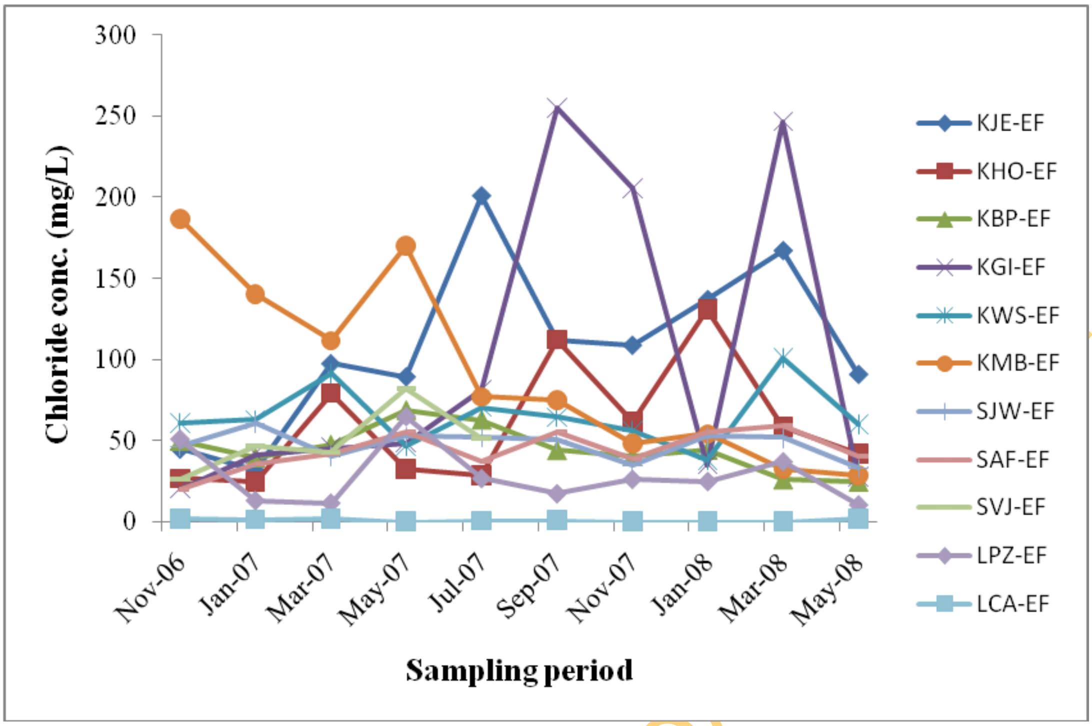

Fig. 4.11: Variations of chloride contents of effluent with sampling period.

effluents. This may be due to low dilution of the effluent and higher production at the various industries.

The chloride levels were higher for wet season for most of the effluents. From November, 2006 to May, 2008, the trend in chloride levels was notably higher for central treatment plant effluents, Galvanizing Industries Limited and May & Baker.

4.3.5 Phosphate and Nitrate

Figure 4.12 and 4.13 show monthly variations of phosphate and nitrate in the effluents respectively. Average phosphate levels for the effluent show no significant difference between the wet and dry season.

Average nitrate levels for the effluent showed significant difference between the wet and dry seasons. The nitrate levels were higher in the wet season than the dry season for most of the effluents. Over 500% highest level of nitrate was observed in September, 2007 in most of the effluents.

4.3.6 Dissolved Oxygen, Biochemical Oxygen Demand and Chemical Oxygen Demand

Dissolved oxygen, biochemical oxygen demand and chemical oxygen demand are very important indicator parameters for the quality of effluents. From Tables 4.19a, 4.20a and 4.21a, seasonal DO levels show no significant difference between the seasons. The levels of DO in the effluents were generally low. This could be as a result of high level of anions and organic pollution in the effluents (D' Amello, 2007). The environmental implication of low DO is the death of aquatic organism in the water body that receives these effluents (Chapelle and Petts, 2004). Figure 4.14 showed monthly variations of DO in the effluents. The DO level is quite low between September, 2007 and May, 2008 for most of the effluents.

Variations in Biochemical Oxygen Demand are shown in Figure 4.15. Significant difference was observed between the wet season and dry season. The level of BOD is lower in the wet season compared to dry season. The low level could be attributed to dilution of the effluents as a result of rain or higher production.

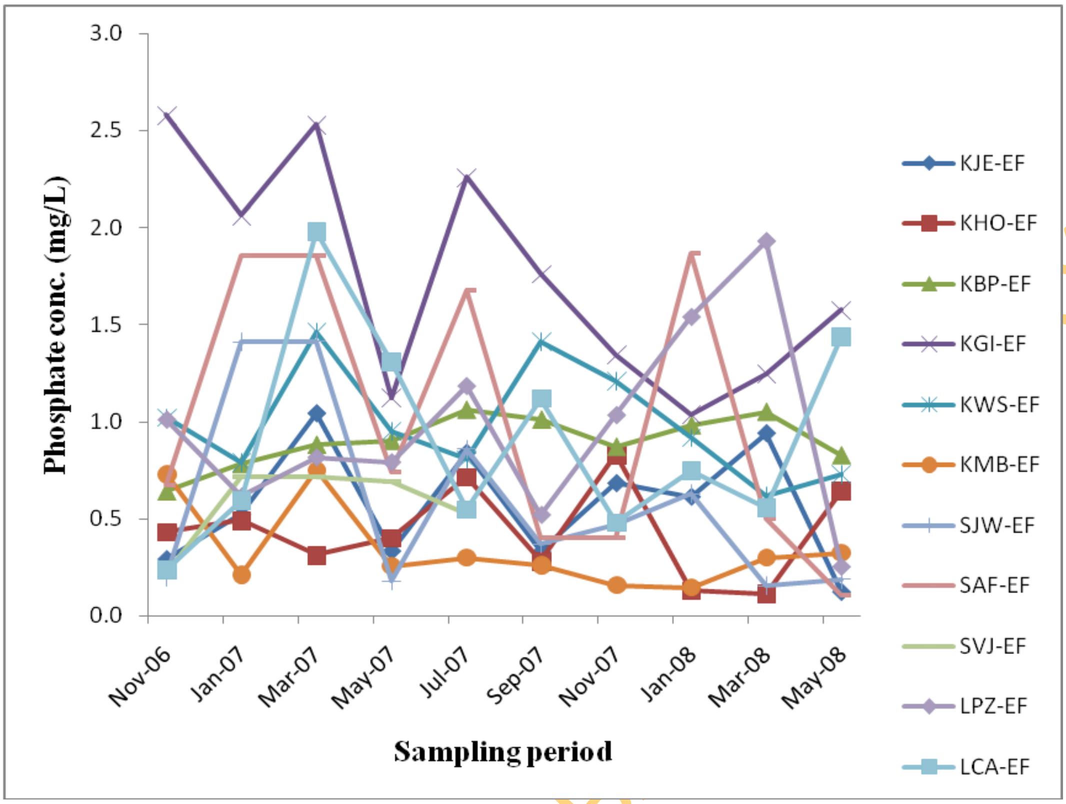

Fig. 4.12: Variations of phosphate contents of effluent with sampling period.

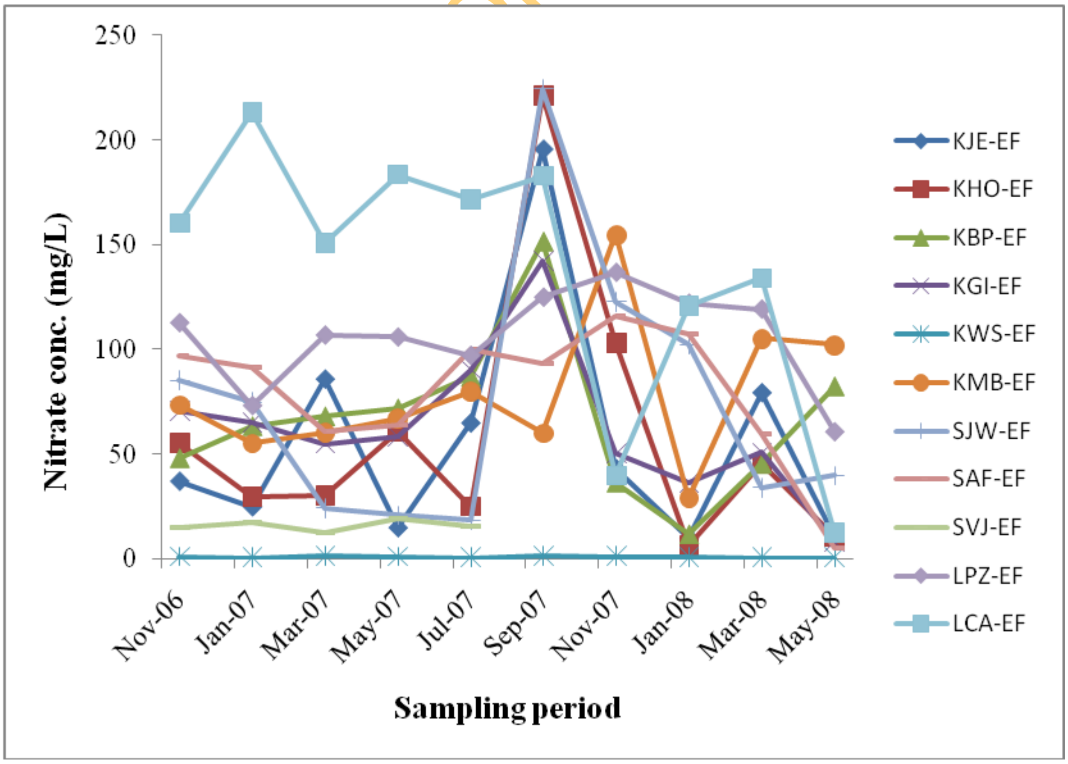

Fig. 4.13: Variations of nitrate contents of effluents with sampling period.

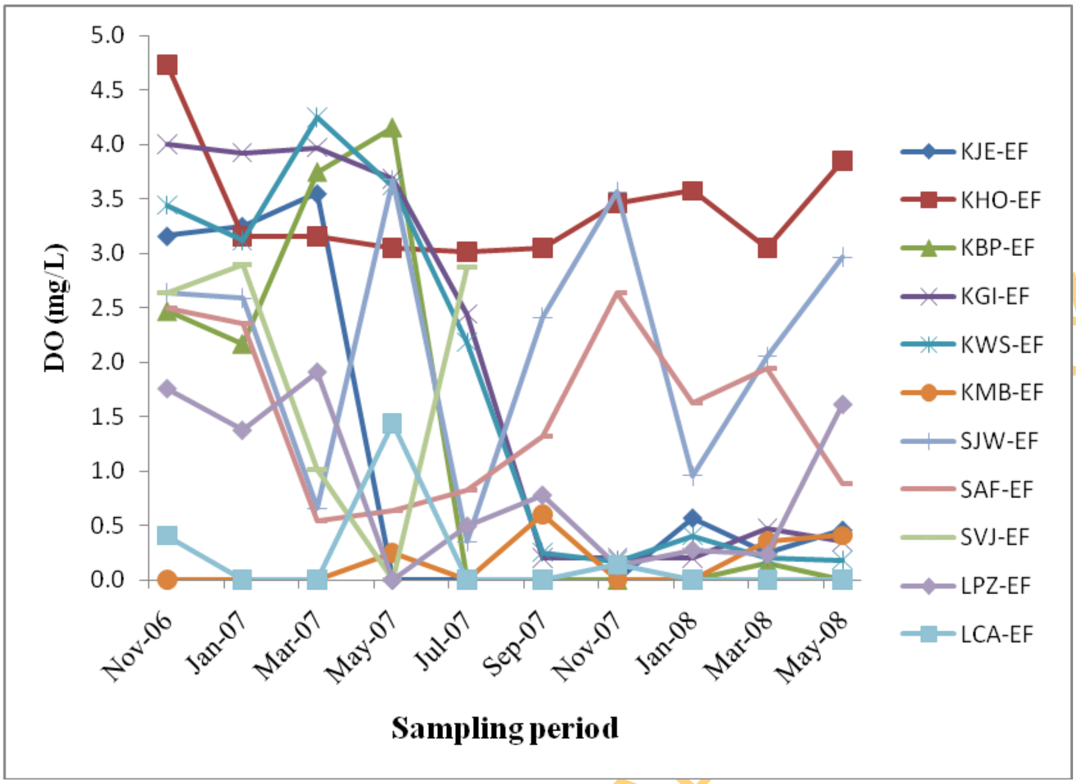

Fig. 4.14: Variations of DO contents of effluents with sampling period.

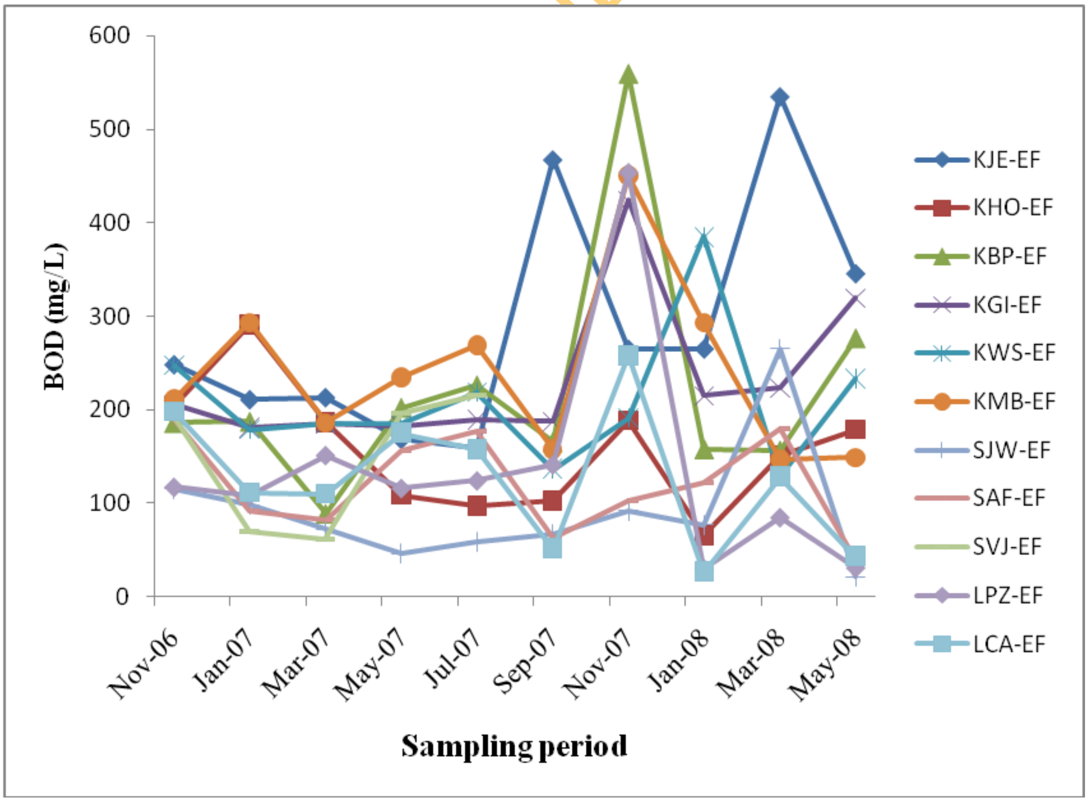

Fig. 4.15: Variations of BOD of effluents with sampling period.

The monthly variations of figure 4.16 show similar trends in COD levels of the effluents as reported for the BOD. Effluents rich in organic and inorganic compounds were responsible for the high levels of COD. An increase in COD levels for most of the effluents was observed in September 2007, November 2007, March 2008, and May 2008 with a decreased level in November 2006, January 2007 and May 2007. Analysis of variance (p = 0.05) showed no significant difference in COD levels during the period of sampling.

4.3.7 Lead

Lead levels were generally higher in the dry season but there were no significant variation observed in the seasons however Woolen & Synthetic Textile Manufacturing Ltd and Berger Paint had higher levels in wet season (Table 4.19b, 4.20b and 4.21b). The dry season levels of lead were higher for other effluents. The number of effluent samples that were below detection limit was 30 out of 105. Figure 4.17 shows the trend of Pb concentrations with time. November 2006, March 2007, May 2007, July 2007, September 2007 and November 2007 showed high Pb concentrations, while January 2007, January 2008, March 2008 and May 2008 showed low Pb concentrations. The seasonal variation is arbitrary in pattern. T-test analysis (p = 0.05) showed no significant difference in Pb levels between the dry season and wet season. Exposure to ambient environmental lead has been associated with a wide range of metabolic disorders and neuropsychological problems especially in children (Fatoki and Ogunfowokan, 2002; Basha *et al*., 2005; Greben et al., 2005; Wu *et al*., 2008).

4.3.8 Cadmium

Cd levels in most of the effluents analysed were higher during the dry season but were no significant variation observed in the seasons (Table 4.19b, 4.20b and 4.21b). About 14 samples out of 105 samples analysed had Cd level below the detection limit. Figure 4.18 shows the variations of Cd concentrations with time. July 2007 and November 2007 showed high Cd concentrations where November 2006, January 2007, March 2007 and May 2007, September 2007, January 2008, March 2008 and May 2008 showed low Cd concentrations. The seasonal variation is arbitrary in pattern. T-test analysis (p = 0.05) showed no significant difference in Cd levels between the dry season and wet season.

4.3.9 Zinc

Zn levels in most of the effluents analysed were higher during the dry season but were no significant variation observed in the seasons**.** (Table 4.19b, 4.20b and 4.21b). None of the

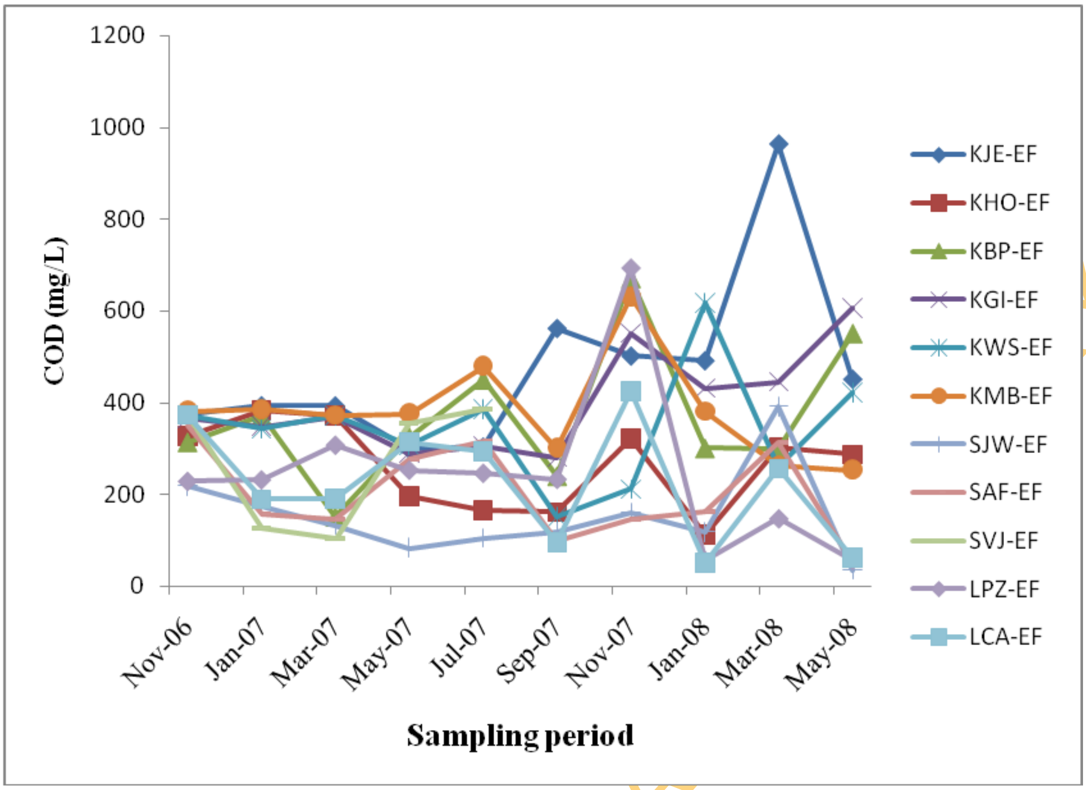

Fig. 4.16: Variations of COD of effluents with sampling period.

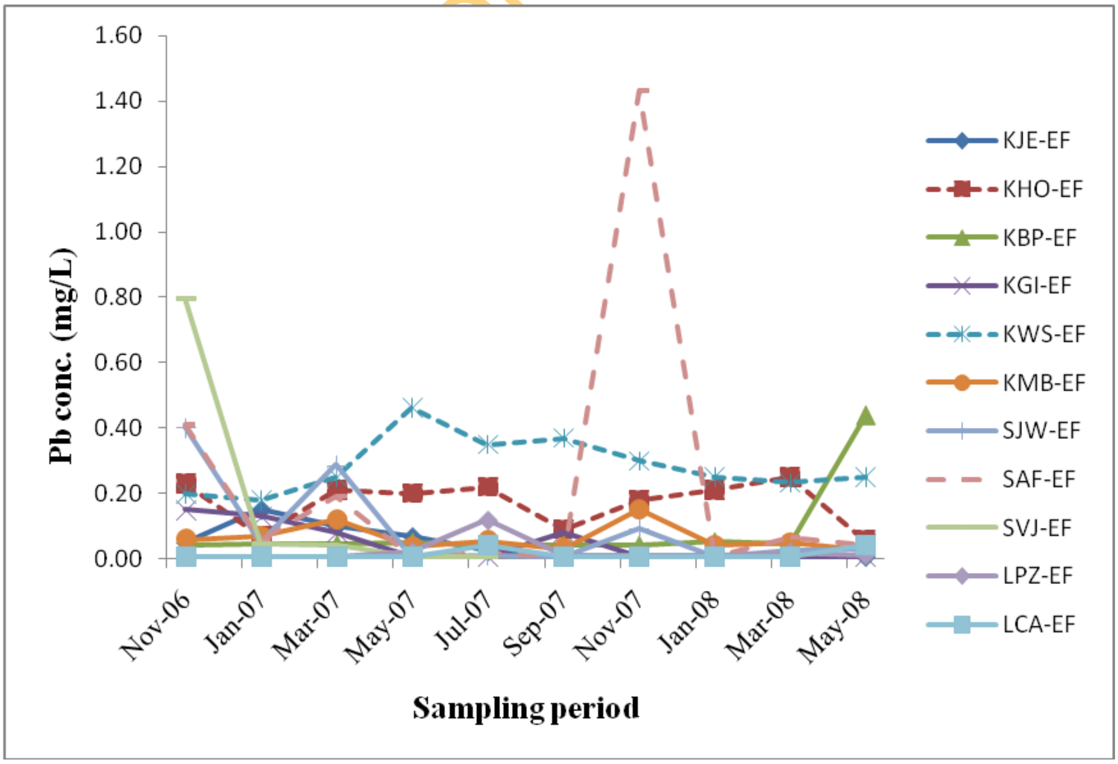

Fig. 4.17: Variations of lead contents of effluents with sampling period.

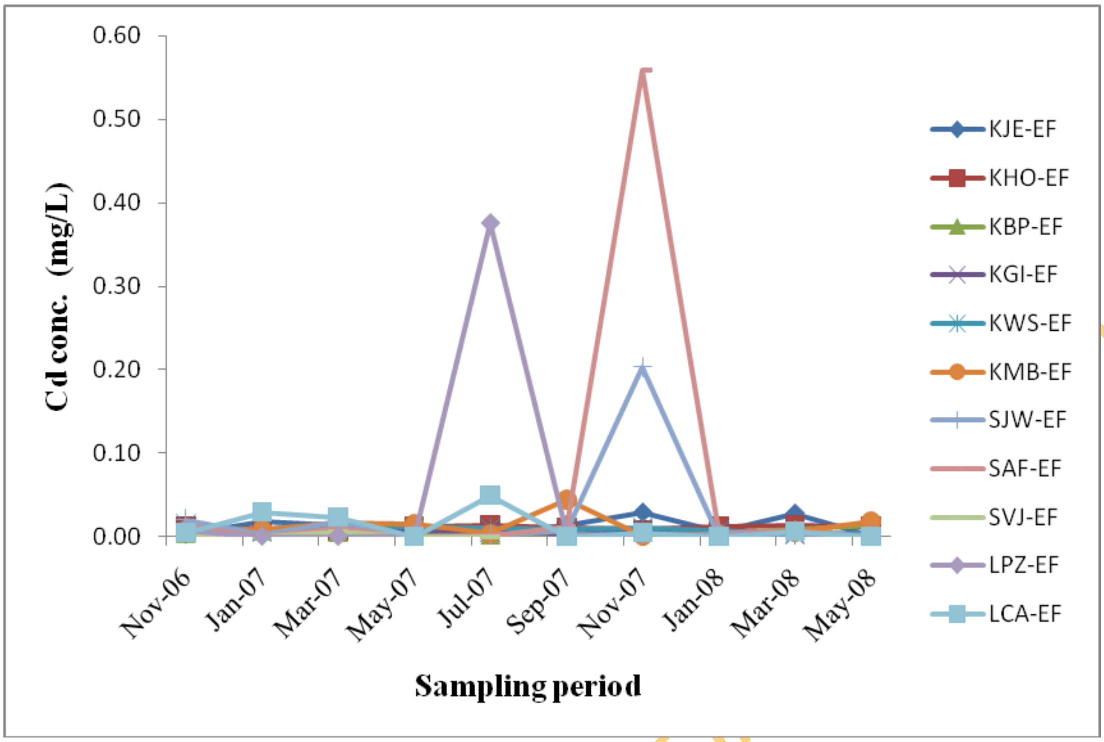

Fig.4.18: Variations of cadmium contents of effluents with sampling period.

effluent samples had Zn level below the detection limit. Figure 4.19 shows the variations in Zn concentrations with time. January 2007, March 2007 and May 2007 showed high Zn concentrations while November 2006, July 2007, September 2007, November 2007, January 2008, March 2008 and May 2008, showed low Zn concentration. T-test analysis ($p = 0.05$) showed no significant difference in Zn levels between the dry season and wet season.

4.2.10 Copper

Copper level in most of the effluents analysed were higher during the wet season compared to dry season. Cu levels (Table 4.19b) for effluents from Woolen & Synthetic Textile Manufacturing limited were not within the regulatory limits for both the wet season (1.5 ± 0.9 mg/L) and dry season (1.4 ±1.0 mg/L). The high levels of Cu in textile effluents could be related to the various dyes used in the manufacturing of textile materials. Figure 4.20 shows the variations in concentrations with time. July 2007 and November, 2007 showed high Cu concentrations where November 2006, January 2007, March 2007, May 2007, September 2007, January 2008, March 2008 and May 2008 showed low Cu concentration. T-Test analysis ($p = 0.05$) showed no significant difference in Cu levels between dry season and wet season.

4.3.11 Chromium

Chromium levels in most of the effluents analysed were higher during the dry season compared to the wet season. Woolen & Synthetic Textile Manufacturing limited had Cr levels (Table 4.19b) high for both the wet season (2.52 ± 0.17 mg/L) and dry season (2.55±0.32 mg/L). About 36 samples out of 105 samples of the effluents analysed had Cr levels below the detection limit. Chromium was not detected in effluents sample of Viju industries Ltd (food and beverages industry). Figure 4.21 shows the trend in Cr concentrations with time. The levels of Cr in both the wet season and dry season seem to be the same in most of the effluents sampled. T-test analysis ($p = 0.05$) showed no significant difference in Cr levels between the dry season and wet season.

4.3.12 Nickel

Nickel levels in most of the effluents analysed were higher during the dry season compared to the wet season. 27 samples of effluents analysed had their levels below the detection limit for Ni. Figure 4.22 shows the trend in Ni concentrations with time. March 2007 and November

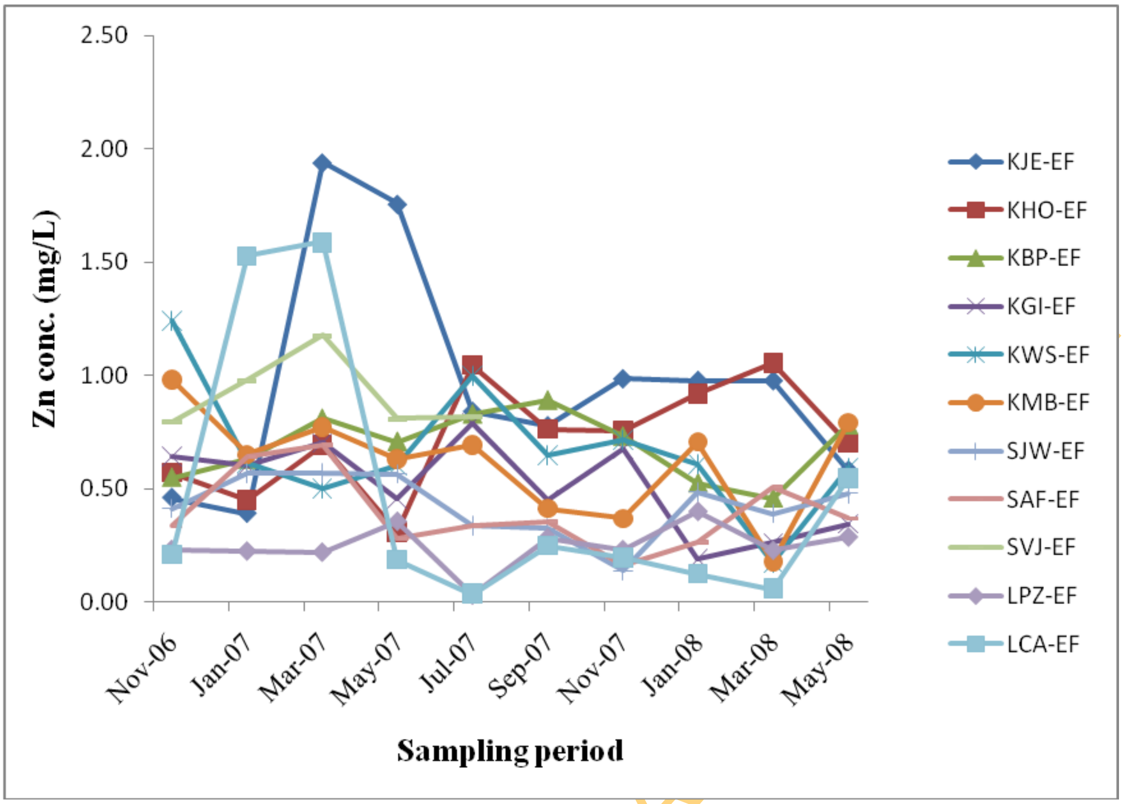

Fig.4.19: Variations of zinc contents of effluents with sampling period.

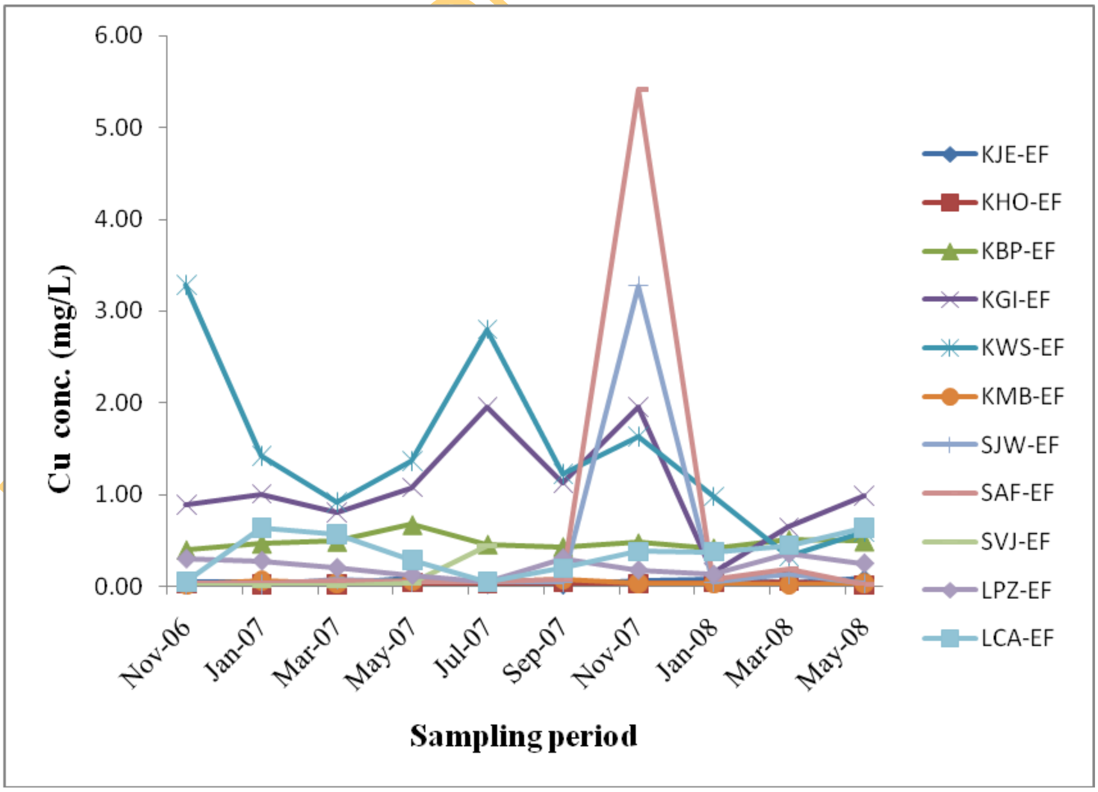

Fig. 4.20: Variations of copper contents of effluents with sampling period.

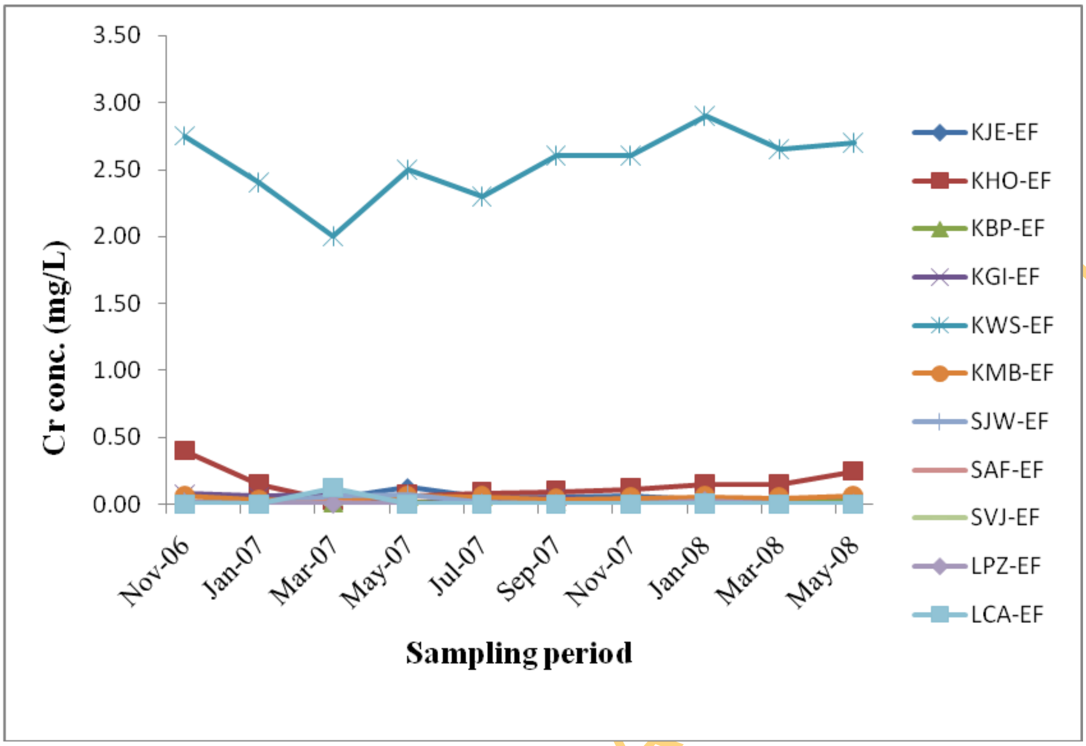

Fig. 4.21: Variations of chromium contents of effluents with sampling period.

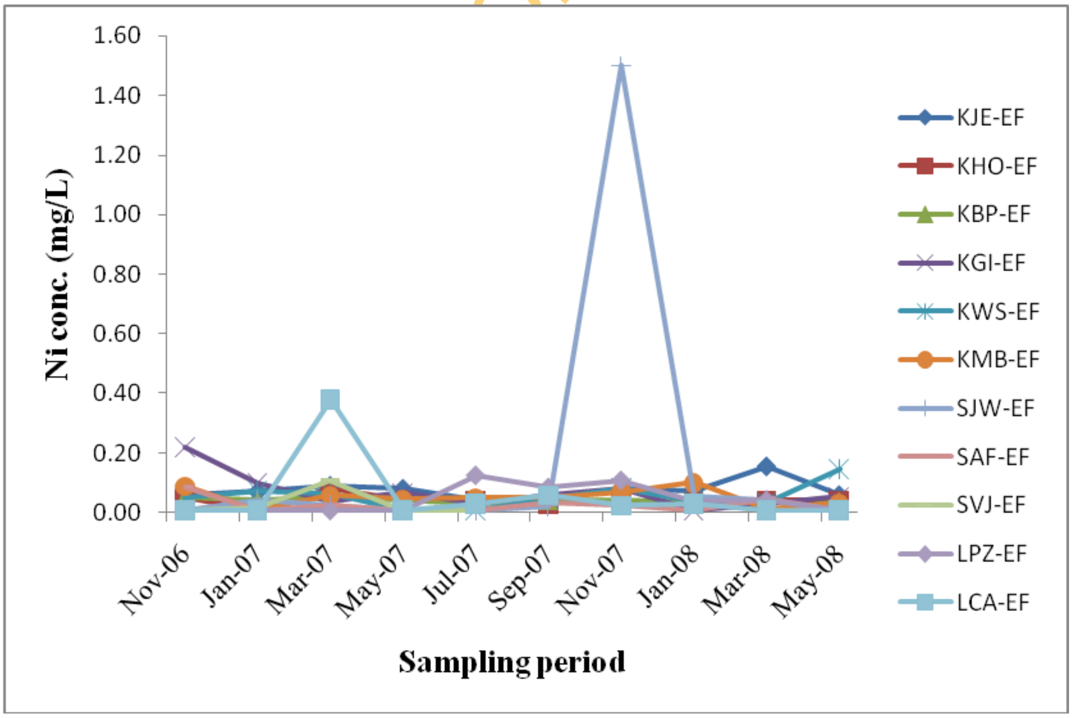

Fig. 4.22: Variations of nickel contents of effluents with sampling period.

2007 showed high Ni concentration while November 2006, January 2007, May 2007, July 2007, September 2007, January 2008, March 2008 and May 2008 showed low Ni concentrations. T-test analysis ($p = 0.05$) showed no significant difference in Ni levels between dry season and wet season.

From the study, it is noticeable that heavy metal levels were higher in the dry season than the wet season. This could be attributed to high volume of production in most of the industries during the dry season and low dilution of the effluents. The low levels of heavy metal in wet season could be associated to dilution of the effluent by rain. It is noteworthy that effluents from textile industry are burden with high level of chromium and copper.

4.4: CHARACTERISTICS OF EFFLUENT CHANNELS SEDIMENTS

Table 4.22 gives the pH, organic matter and particle size characteristics of sediments from effluents channel around Ikeja, Isolo and Ilupeju Industrial Estates while Table 4.23 gives the levels of metals in sediment from effluents channel around Ikeja, Isolo and Ilupeju Industrial Estates.

The sediments were predominantly sandy with low % organic matter. The sandy nature is comparable to the particle size in the soil around the industrial areas. The range of sediments pH were 4.2-6.7 for KJE-SD and 6.7-7.5 for KHO-SD in Ikeja industrial estate, 6.1-6.5 for SVJ-SD in Isolo industrial estate, while 6.7-7.0 for LPZ-SD and 6.3 - 7.3 for LCA-SD in Ilupeju industrial estate. The low pH values of KJE-SD sediment (5.8±0.8) may allow the release of some toxic metals that would otherwise be adsorbed to sediment (Mouvet and Borg, 1983). The high levels of heavy metals in the effluents channel in KJE could have contributed in the elevated level of metals in the sediment (Table 4.1). pH variation in sediments influences the release or adsorption of each metal into sediment fraction. High pH lowers desorption of metals and possesses high buffering capacity against acidic conditions that may be created as a result of wastes accumulation. Association of metals with the carbonate, Fe-Mn-Oxides and organic fraction are affected by pH variations (Ikem *et al.*, 2003). Cd, Cu and Zn are mostly bound to carbonate and Fe-Mn oxides fraction. Low pH is known to influence the sorption of Pb by organic fraction in sediments (Bodar *et al.*, 2006; Vamerali *et al.*, 2010).

Table 4.22: pH, organic matter and particle size characteristics of sediments from effluent channel around Ikeja, Isolo, Ilupeju industrial estates.

Site Code		**pH**	**Organic Carbon (%)**	**Organic Matter (%)**	**Sand (%)**	**Clay (%)**	**Silt (%)**
KJE-SD	Mean	5.8±0.8	2.4±1.3	4.2±2.2	92.8 ±1.8	4.0 ±1.2	3.2±1.1
	Range	4.2-6.7	1.0-4.0	1.8-7.0	90.2-95.7	2.6-5.4	1.7-4.9
KHO-SD	Mean	7.0±0.2	3.5±0.7	6.2±1.6	92.0±1.7	2.9±0.8	5.2±1.2
	Range	6.7-7.50	2.0-4.5	3.5-9.8	90.2-95.5	1.9-4.4	3.0-6.9
SVJ-SD	Mean	6.3±0.1	2.7±0.2	4.6±0.3	92.2±0.9	4.5±0.8	3.3±0.8
	Range	6.1-6.5	2.6-3.0	4.4-5.1	91.2-93.5	3.3-5.2	2.6-4.3
LPZ-SD1	Mean	6.4±0.2	2.2±1.0	3.8±1.7	94.1±1.5	2.3±0.9	3.7±1.0
	Range	6.2-6.9	0.7-3.1	1.1-5.3	91.7-95.9	1.0-4.0	2.4-5.3
LPZ-SD2	Mean	6.1±0.2	2.5±0.7	4.5±2.0	93.6±0.6	2.1±0.6	4.3±0.5
	Range	5.9-6.4	1.8-4.0	3.2-8.8	92.9-94.7	1.0-2.9	3.4-5.2
LPZ-SD3	Mean	6.1±0.2	1.8±1.4	3.2±2.5	95.0±1.0	2.3±0.5	3.7±3.7
	Range	5.9-6.6	0.4-3.9	0.6-6.7	93.1-96.1	1.9-2.9	1.9-14.0
LPZ-SD	Mean	6.3±0,3	2.0±1.0	3.5±1.9	94.3±0.8	2.3±0.5	3.5±0.6
	Range	6.1-7.0	0.6-3.5	1.1-6.7	92.9-95.5	1.6-2.9	2.4-4.5
LCA-SD1	Mean	6.8±0.5	1.4±1.1	2.5±1.9	86.0±1.6	8.3±1.2	5.7±1.4
	Range	6.1-7.4	0.3-4.0	0.6-6.8	83.9-88.7	6.9-10.0	4.4-8.1
LCA-SD2	Mean	6.8±0.3	1.1±1.1	1.9±1.9	85.7±1.7	8.6±1.1	5.5±1.1
	Range	6.4-7.2	0.2-4.0	0.3-6.8	83.7-88.7	7.0-10.9	4.3-7.4
LCA-SD	Mean	6.8±0.4	1.3±1.1	2.2±1.8	85.9±1.5	8.4±1.1	5.6±1.1
	Range	6.3-7.3	0.3-4.0	0.5-6.8	84.3-88.7	7.0-10.5	4.4-7.3

Table 4.23: Concentrations of metals (µg/g) in sediments from effluent channel around Ikeja, Isolo, and Ilupeju industrial estates.

Site Code		Lead	Cadmium	Zinc	Copper	Chromium	Nickel
KJE-SD	Mean	80± 39	13±4.3	2210 ±500	128±62	31±11	34±10
	Range	31-150	7.8-23.2	1440-3270	87-244	12-49	21-55
KHO-SD	Mean	453±320	19.9±1.4	2200±320	49 ±5	28±7	22±6
	Range	229-1127	16.4-21.7	1460-2440	44-56	17-39	17-33
SVJ-SD	Mean	46±33	0.43±0.26	326±82	70±15	15.8±2.3	6.5±3.5
	Range	10-93	0.14-0.66	196-423	57-92	13.1-19.1	2.6-10.2
LPZ-SD1	Mean	165±34	1.0±0.4	257±46	74±28	20±3	10±4
	Range	121-218	0.3-1.6	208-327	33-115	14-26	4.5-16.6
LPZ-SD2	Mean	71±30	0.7±0.5	226±9	92±57	13±4	8±4
	Range	35-129	0.2-1.6	211-237	25-201	6.7-18.7	4.4-16.3
LPZ-SD3	Mean	62±34	1.2±1.2	231±47	65±20	18±5	9±4
	Range	32-134	0.2-4.5	179-353	38-101	11.7-27.3	4.2-13.3
LPZ-SD	Mean	105±27	1.0±0.6	242±18	75±27	18±4	9±3
	Range	67-165	0.4-2.4	223-280	33-115	12.2-24.6	4.7-14.8
LCA-SD1	Mean	155±20	0.9±0.4	271±61	71±30	18±6	10±3
	Range	127-182	0.4-1.5	221-404	27-115	10.2-27.2	6.1-15.7
LCA-SD2	Mean	149±20	0.8±0.5	328±80	69±43	20±9	12±3
	Range	127-195	0.2-1.7	238-476	21-162	11-33	6.51-15.8
LCA-SD	Mean	152±16	0.9±0.4	300±59	70±31	19±7	11±2
	Range	132-188	0.4-1.3	237-414	27-131	11.1-28.1	6.4-14.7

It was observed that the levels of the heavy metals studied were highest in KHO-SD; this could be due to the high organic matter content and the pH of the sediment since organic matter has been found to influence heavy metal adsorption in sediments. The levels of heavy metals in sediments studied were in the order of Zn> Pb > Cu> Cr>Ni> Cd (Table 4.23).

Table 4.24 shows the Pearson correlation coefficient between the pair of parameters determined in the effluent channels. There were weak correlations between pairs of heavy metals. ANOVA at 95% confidence limit showed no significant difference among the parameters for pH, Cu, % sand, %clay and %silt, while Pb, Cd, Zn, Cr and Ni.

4.4.1: Lead

Levels of Pb were highest in KHO-SD (453±320 µg/g) followed by LCA-SD (152 ±16 µg/g) and LPZ –SD (105±27 µg/g) (Table 4.23). The levels are about 13, 15 and nine folds; four,five and three folds; three, three and two folds greater than the average level in sediment quality guidelines (CCME,1995; MOEE,1993 and ANZECC/ARMCANZ,2000) respectively. The results obtained for KHO-SD and LPZ –SD are greater than report by (Ajibola, and Ladipo, 2011) on the levels of Pb in sediment effluent channels of PZ (56±46 µg/g) and steel industry (69±27 µg/g). The high levels of this metal in sediment could be related to the type of raw materials utilize in the manufacturing process. The high degree of Pb in the sediment will have a negative effect on aquatic life. This effect will arise when metals are released into the water column; hence bioconcentrates in the skin, bones, kidneys, and liver of fish (Falconer, 1999). Also when lead concentrations in algae exceed 500 ppb, enzymes needed for photosynthesis are inhibited. When less photosynthesis takes place, the algae will produce less food and therefore will not grow as much. Reduction in algal growth leads to less food for animals; this has negative effect on the entire ecosystem. Fish are more sensitive to high lead concentrations than algae. When lead levels exceed 100 ppb, gill function is affected (Falconer, 1999). Embryos and fry are more sensitive to the toxic effects of lead than the adult fish (Falconer, 1999). Lead is more toxic at lower pH and in soft water (Falconer, 1999; Wright and Welbourn, 2002).

The increase in the levels of Pb was in the order of KHO-SD > LCA-SD > LPZ-SD > KJE-SD > SVJ-SD. The levels of Pb were higher in the sediments compared with the levels in the soil around the industrial estates.

Table 4.24: Pearson correlation coefficient results between parameters determined in effluent channel sediments.

	pH	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**	**OC**	**OM**	**Sand**	**Clay**	**Silt**
pH	1											
Pb	.465[b]	1										
Cd	0.183	0.543[b]	1									
Zn	0.040	0.400[b]	0.926[b]	1								
Cu	-0.261[a]	-0.192	0.090	0.248[a]	1							
Cr	-0.009	0.209	0.552[b]	0.616[b]	0.212	1						
Ni	-0.123	0.125	0.717[b]	0.790[b]	0.331[b]	0.709[b]	1					
OC	-0.058	0.338[b]	0.406[b]	0.371[b]	0.172	0.026	0.171	1				
OM	-0.038	0.367[b]	0.405[b]	0.367[b]	0.155	0.009	0.171	0.990[b]	1			
Sand	-0.457[b]	-0.097	0.169	0.140	0.034	0.102	0.107	0.258[a]	0.255[a]	1		
Clay	0.389[b]	-0.033	-0.238[a]	-0.178	0.007	-0.131	-0.091	-0.343[b]	-0.334[b]	-0.933[b]	1	
Silt	0.292a	0.198	-0.008	-0.054	-0.032	-0.127	-0.106	0.132	0.115	-0.552[b]	0.326[b]	1

[a] Significant at the 0.05 level.

[b] Significant at the 0.01 level.

4.4.2: Cadmium

The Cd ranged between 16.4 µg/g and 21.7 µg/g with mean values of 19.9±1.4 µg/g for KHO-SD (Basic metal industry type) while the SVJ-SD (Food & Beverage) ranged within 0.14-0.66 with mean values of 0.43±0.26 µg/g. The concentrations of Cd in sediments from industrial channels in Ikeja industrial Estate were higher than the corresponding soil (Table 4.29). This reflects the effect of sediments as a sink for metals. The levels of Cd in LPZ-SD and LCA-SD from effluent channels in Ilupeju industrial estate were 1.0±0.6 µg/g and 0.9±0.4 µg/g respectively.

The levels in KJE-SD, KHO-SD, SVJ-SD, LPZ-SD and LCA-SD were about 22 and 8; 33 and 13; one respectively; 2 and 1; 2 and 1 folds greater than the average level in sediment quality guidelines (CCME, 1995 and ANZECC/ARMCANZ, 2000) respectively. The increase in the levels of Cd are in the order of KHO-SD > KJE-SD> LPZ-SD > LCA-SD > SVJ-SD.

4.4.3: Zinc

The level of Zn in KJE-SD (effluent channels from Ikeja Industrial Estate) was highest with value 2213±504 µg/g while the lowest value was obtained from LPZ-SD (effluent channels from Ilupeju Industrial Estate) 242±18 µg/g. The high level of Zn concentration in the effluent channels from Ikeja industrial estate could be associated to anthropogenic sources. The concentration of Zn was higher in the soil quality studied from Ikeja industrial area compared to the soil quality from other industrial estates. The results obtained for KHO-SD (2200±320 µg/g) and LPZ –SD (242±18 µg/g) are greater than report gave by (Ajibola and Ladipo, 2011) on the levels of Zn in sediment effluent channels of PZ (141±54 µg/g) and steel industry (614±380 µg/g). The levels in KJE-SD, KHO-SD, SVJ-SD, LPZ-SD and LCA-SD were 18 and 11; 18 and 11; 3 and 2; 2 and 2; 2 and 2 folds greater than the average level in sediment quality guidelines (CCME, 1995 and ANZECC/ARMCANZ, 2000) respectively. The increase in the levels of Zn was in the order of KJE-SD >KHO-SD > SVJ-SD > LCA-SD > LPZ-SD. The high concentration of Zn though not usually a cause for human health have greater impacts in the health of aquatic ecosystem.

4.4.4: Copper

Copper concentrations in the sediments are in the decreasing order of KJE-SD (128±62µg/g); LPZ-SD (75±27); LCA-SD (70±31µg/g); SVJ-SD (70±15µg/g); and KHO-SD (49±5). The average Cu content in soils/sediments is considered to be about 30 mg/kg (Adriano, 2001). The levels in sediment studied are greater than the average kevel. The levels of Cu in sediments channel of Ikeja Industrial Estate (KJE-SD and KHO-SD) are higher than the levels in soils around the estate (Table 4.29). Variations in the concentrations of the metals examined reflect anthropogenic input from the industries. The results obtained for LPZ –SD (75±27 µg/g) is greater than report by (Ajibola, and Ladipo, 2011) on the levels of Cu in sediment effluent channels of PZ (22.4±8.8 µg/g) while KHO-SD (49±5 µg/g) is less than the steel industry (73±18 µg/g). The levels in KJE-SD, KHO-SD, SVJ-SD, LPZ-SD and LCA-SD were about 4, 8 and 2; 1, 3 and 1; 2, 4 and 1; 2, 5 and 1; 2, 4 and 1folds greater than the average level in sediment quality guidelines (CCME, 1995; MOEE, 1993 and ANZECC/ARMCANZ, 2000) respectively. Although copper toxicity in humans is rare, aquatic organisms are potentially at risk from Cu exposures (Adriano, 2001).

4.4.5: Chromium

The Cr ranged between 12 µg/g and 49 µg/g with mean values of 31±11 µg/g for KJE-SD (Central treatment plant) while the LCA-SD (effluent channels from Ilupeju Industrial Estate) ranged between 6.4-14.7 µg/g with mean values of 11±2 µg/g. The average Cr concentration in soils/sediments was reported to be 40-50 mg/kg (Adriano, 2001). All the sediment samples had lower Cr concentrations than the average reported by Adriano (2001). The results obtained for LPZ -SD (18±4 µg/g) and KHO-SD (basic metal) (28±7 µg/g) are lower than report gave by (Ajibola, and Ladipo, 2011) on the levels of Cr in sediment effluent channels of PZ (144±24 µg/g) and steel industry (146±23 µg/g). The levels in KJE-SD, KHO-SD, SVJ-SD, LPZ-SD and LCA-SD were about one fold greater than the average level in sediment quality guidelines (CCME, 1995 and MOEE, 1993 sediment qualities) for all the sediments studied respectively. The levels of Cr in the sediments were higher than the levels in the soil around the estates. Variations in the concentrations of the metals examined reflect anthropogenic input from the industries. The levels of Cr in the sediments are in the order of KJE-SD >KHO-SD > LPZ-SD > SVJ-SD > LCA-SD.

4.4.6: Nickel

The level of Ni in KJE-SD (effluent channels from Ikeja Industrial Estate) was highest with mean value 34±10 µg/g while the lowest mean value was obtained from SVJ-SD (Food & beverages) 6.5±3.5 µg/g. The average Ni concentration in soils/sediments is reported as 20 mg/kg. All the sediment samples except KJE-SD and KHO- SD had lower Ni concentrations than the average reported by Adriano (2001). However, Ni is relatively less toxic to invertebrates; it can be toxic to aquatic organisms such as reduction in skeletal calcification and diffusion capacity of gills (Moore, 1991). The sediments from KJE-SD and KHO- SD may affect fish when eventually discharged into the water bodies. The results obtained for LPZ -SD (9±3 µg/g) and KHO-SD (22±6 µg/g) are lower than report gave by (Ajibola, and Ladipo, 2011) on the levels of Ni in sediment effluent channels of PZ (41±28 µg/g) and steel industry (107±41 µg/g). The levels in KJE-SD (two folds), while others (KHO-SD, SVJ-SD, LPZ-SD and LCA-SD) are one fold greater than the average level in (MOEE, 1993) quality guideline. The levels of Ni in the sediments were higher than the levels in the corresponding soils around the various estates. The levels of Ni in the sediments are in the order of KJE-SD >KHO-SD > LCA-SD > LPZ-SD > SVJ-SD.

Generally, the concentrations of metals in the sediment were higher in effluents channels from Ikeja industrial estates compared with other studied estates.

4.5 MULTIVARIATE ANALYSIS OF HEAVY METALS DISTRIBUTION IN SEDIMENTS.

In order to reduce the relatively large number of variables to a smaller number of orthogonal factors, the original data obtained was processed by multivariate statistical methods. The distribution pattern of individual associations of elements in sediments were determined by Principal Component Analysis and Correspondence Analysis (CA).

Table 4.25 shows the eigen values from the PCA of the sediments analysed. Based on the eigen values, the first two factors with the highest values were used. The two factors explained 96.3% of the total variance. The first factors explained 69.4% of the total variance which was strongly and positively related to Pb and Cd while the second explaining 26.9% of the total variance showed negative loadings in Zn, Cr, Ni and Cu as shown in Figure 4.23. The first component which accounts for 69.4% variance indicates that points KJE-SD and KHO-SD had elevated levels of total metals levels. As shown from figure 4.23, the points were not clustered meaning that there were variations in metal levels in sediments for the various points. This could be as a result of various industrial processes. Points to the left SVJ-

Table 4.25: Principal component analysis of sediments for heavy metal data.

Factor	**Initial Eigen Values**	**Percentage Variance**	**Cumulative Percentage**
1	3.788	69.39	69.39
2	1.470	26.92	96.31
3	0.116	2.12	98.43
4	0.078	1.43	99.86
5	0.005	0.09	99.95
6	0.002	0.04	100

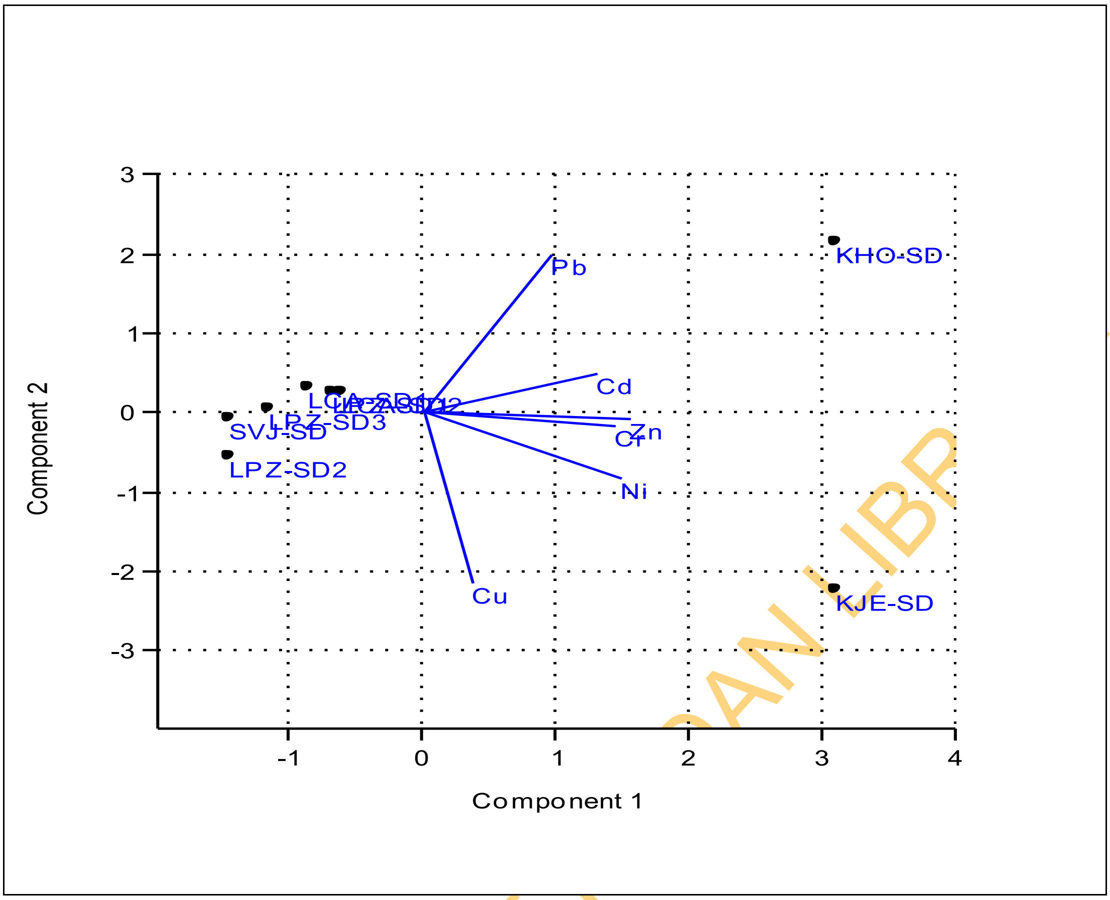

Fig. 4.23: Principal component bi-plot of sediment metal data.

SD, LPZ-SD1, LPZ-SD2, LPZ-SD3, LCA-SD1 and LCA-SD2 from the origin indicate low levels of Pb, Cd, Zn, Cu, Cr and Ni while points on the right KJE-SD and KHO-SD of the origin indicate high levels of Pb, Cd, Zn, Cu, Cr and Ni.

Figure 4.24 shows the CA relay plot of the categorisation result of the heavy metals which confirm that Zn and Cd are anthropogenic by source and Ni, Cr, Pb and Cu from geological bedrock formation.

The Hierarchical cluster analysis (HCA) were classified into three clusters (Figure 4.25).There were three sites in cluster 1 (SVJ-SD, LPZ-SD2, LPZ-SD3), three sites in cluster 2 (LPZ-SD1, LCA-SD1, LCA-SD2) and two sites in cluster 3 (KJE-SD, KHO-SD).

The decreasing pollution order of heavy metal concentrations in the effluent channel sediments are Cluster 3 > cluster 2 > cluster1. From the statistical analysis, it was established that sediments samples from effluent channels from Ikeja industrial area had highest concentration of heavy metal.

4.6. COMPARISON OF METALS IN SEDIMENTS WITH SEDIMENT QUALITY GUIDELINES.

Table 4.26 shows the levels of the metals studied compared to Canadian sediment quality guidelines, Ontario sediment quality guidelines and Australian sediment Quality Guidelines. Pb levels in SVJ-SD are less than Australian sediment Quality Guidelines but greater than the other two quality guidelines. The other sediments studied had the levels of Pb greater than Canadian sediment quality guidelines and Ontario sediment quality guidelines. Cd in SVJ-SD sediment is lower than the three quality standard guidelines, while LPZ-SD and LCA-SD are lower than Australian sediment Quality Guidelines. Cr levels in all the sediments are lower than the sediment quality standard guidelines while Ni in SVJ-SD; LPZ-SD and LCA-SD are lower than the Ontario sediment quality guidelines.

Generally, the sediments studied had Pb, Cd, Zn, and Cu higher than the sediment quality guidelines.

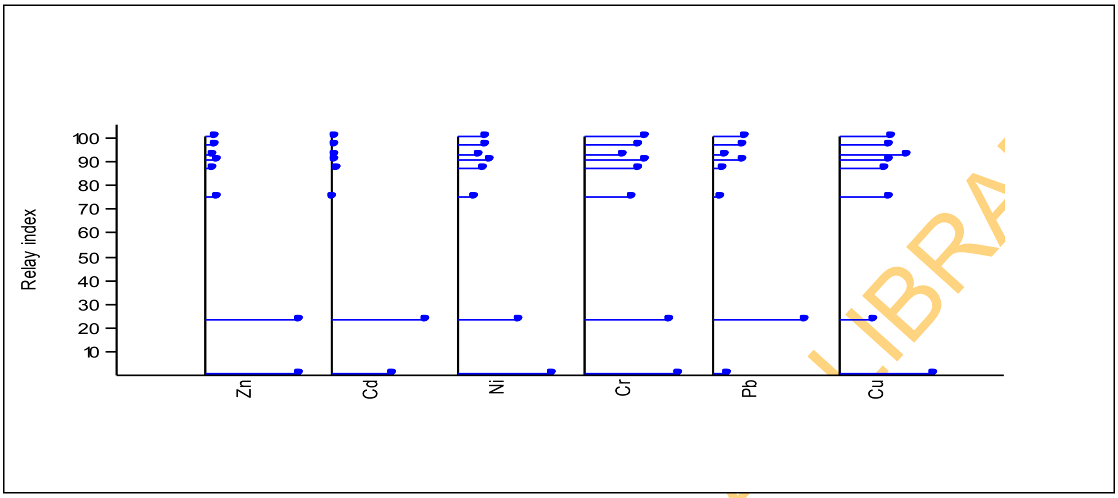

Fig. 4.24: Correspondence analysis relay plot of sediments for six metals.

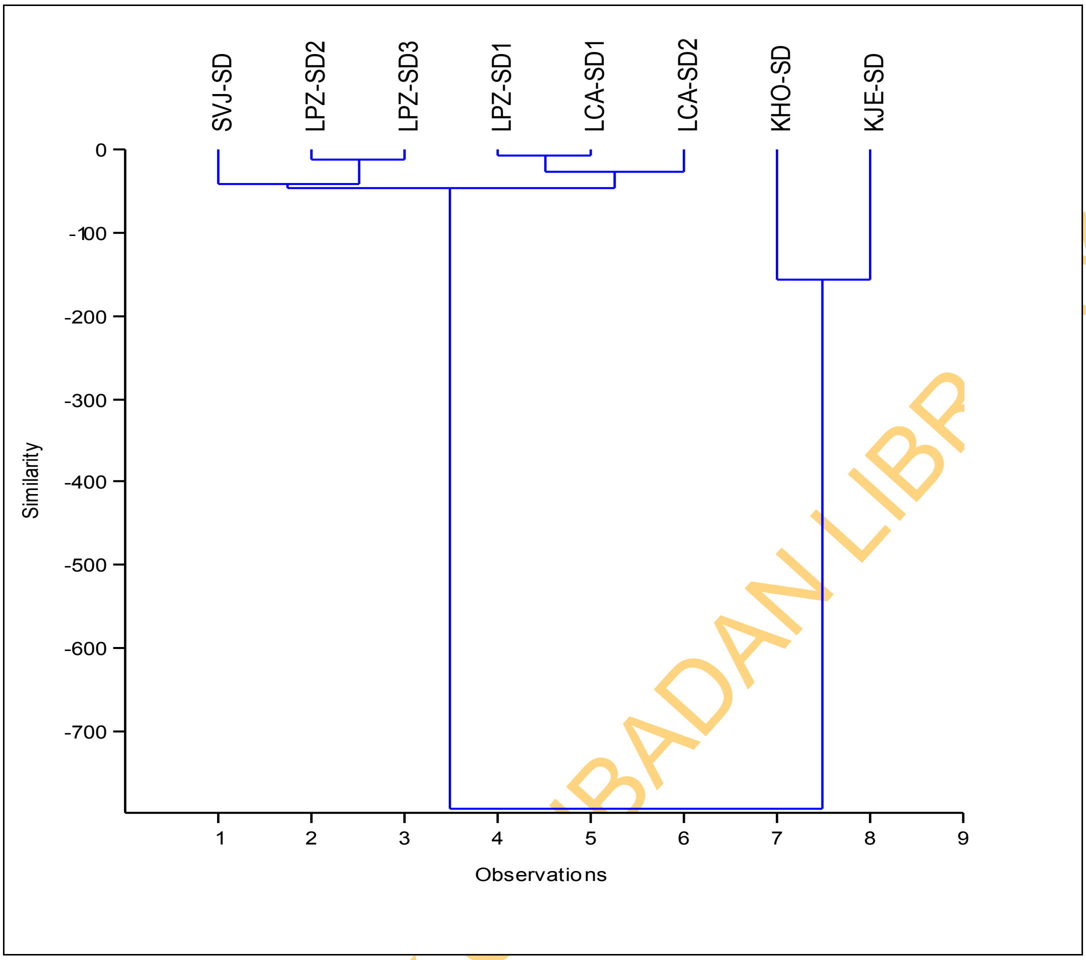

Fig 4.25: Hierarchical cluster analysis dendrogram for sediment samples.

Table 4.26: Comparison of heavy metals in sediment channel with sediment quality guidelines.

Site Code	**This Study**					**Canada** (CCME, 1995)	**Canada-Ontario** (MOEE, 1993)	**Australia & New Zealand** (ANZECC/ ARMCANZ, 2000)
	KJE-SD	**KHO-SD**	**SVJ-SD**	**LPZ-SD**	**LCA-SD**			
Pb	80	453	46	105	152	35	31	50
Cd	13	19.9	0.43	1	0.9	0.6	0.6	1.5
Zn	2210	2200	326	242	300	123	120	200
Cu	128	49	70	75	70	35.7	16	65
Cr	31	28	15.8	18	19	37.3	26	NA
Ni	34	22	6.5	9	11	NA	16	NA

NA- not available

4.7 CORRELATION OF METALS IN EFFLUENTS AND SEDIMENT

Heavy metals are natural constituent in sediments but due to industrialization, the levels have increased greatly. The contamination of sediments of water bodies is one of the worst problems in the environment due to the sediment acting as both a sink and a source for heavy metal to aquatic system. The sediments along the effluent channels reflected significant level of heavy metal accumulation when compared to levels in the effluent. The heavy metals analysed for effluents and sediments showed positive significant correlations for Zn ($r = 0.644$) and Cr ($r = 0.748$) while Pb ($r = 0.404$) and Ni ($r = 0.464$) showed low positive significant correlations as shown in (Table 4.27). This shows that Zn and Cr in the effluent and sediments originated from a similar source. Therefore means that, these metals levels in sediments are anthropogenic in nature.

4.8: SOIL QUALITIES AROUND THE EFFLUENT CHANNELS

4.8.1. Characteristics of Soil around Ikeja industrial estate

The pH of soil in Ikeja industrial estate ranged between 6.4 and 8.5, while the control sample pH for Ikeja industrial estate ranged within 6.2-7.8. The soil pH in Ikeja industrial estate was near neutral. The % organic matter in Ikeja soil ranged between 0.7 and 7.1 while points KBP-SL1 and KMB-S4 had very high organic matter content for all the months sampled. % sand ranged between 75.2 and 97.2, while point KBP-SL1 had the highest means value 95.0±2.0 for all the period sampled. % clay and % silt ranged between 1.7 and 10.0 and 0.2 and16.9 respectively while KMB-SL4 had the highest value of % clay and % slit for all the period of sampled (Table 4.28).

Pb concentrations were found to be quite high, ranging from 5 µg/g - 217 µg/g. Point KGI-SL2 had the highest concentration of 100±70 µg/g (Table 2.29) At this point it was observed that the sediments from the effluent channel are often excavated to the surface top soil. Cd concentration was found to be high. The concentrations ranged from 0.3µg/g-5.1µg/g, with KMB-S4 having the highest concentration of 3.0±1.3 µg/g.

The high level of Cd in the soil could also be attributed to overflow of effluent from KMB-EF channel to the surface of the road. The highest concentration of Cd was observed in KMB-EF.

Table 4.27: Correlation coefficient (p=0.05) for heavy metal levels in sediment/effluent.

Heavy metals	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**
Coefficient	0.404	-0.251	0.644*	-0.279	0.748*	0.461

* strong correlation.

Table 4.28: pH, organic matter and particle size characteristics of soil from Ikeja Iindustrial Estate.

Site Code		**pH**	**Organic Carbon (%)**	**Organic Matter (%)**	**Sand (%)**	**Clay (%)**	**Silt (%)**
KBP-SL1	Mean	6.4±0.4	2.0±1.4	3.0±2.5	95.0±2.0	3.1±0.8	2.5±1.4
	Range	5.8-6.9	0.6-4.10	0.7-70	91.5-97.2	2.2-4.8	0.2-47
KGI-SL2	Mean	6.2±0.6	3.1±1.1	5.4±2.0	91±2.5	2.6±1.0	6.3±2.2
	Range	5.0-6.9	0.7-41	1.2-7.1	85.9-93.2	2.0-5.0	3.7-10.1
KWS-SL3	Mean	6.5±0.7	2.4±0.8	4.1±1.3	89.7±4.3	5.1±2.3	5.3±2.2
	Range	5.6-7-8	1.0-3.7	1.7-6.4	84.7-95.8	2.0-8.2	2.1-8.4
KMB-SL4	Mean	7.5±0.3	2.5±1.1	4.3±1.9	86.8±7.7	5.9±3.3	7.5±`4.9
	Range	7.0-7.9	0.6-4.1	1.1-7.1	75.2-96.5	1.7-10.0	1.4-16.9
K-SL	Mean	7.3±0.7	2.5±0.9	4.4±1.6	93.4±9.6	4.3±1.6	5.6±2.5
	Range	6.4-8.5	0.8-4.2	1.3-7.4	86-118.7	2.4-6.3	2.4-8.6
K-CTR-SL1	Mean	7.3±0.5	1.0±0.4	1.6±0.6	88.8±4.3	5.5±2.5	5.7±2.6
	Range	6.2-7.8	0.6-1.6	1.0-2.8	83.2-94.2	2.3-9.9	2.0-10.1
K-CTR-SL2	Mean	7.3±0.5	1.0±0.2	1.7±0.4	90±3.4	4.8±1.8	4.9±2.5
	Range	6.2-7.8	0.7-1.3	1.2-2.2	86.2-95.5	2.9-8.0	1.3-8.7
	Mean	7.3±0.5	1.0±0.3	17±0.5	89.6±3.7	5.2±2.1	5.3±2.5
K-CTR-SL	Range	6.2-7.8	0.7-1.5	1.1-2.5	85.0-94.4	2.6-8.9	1.9-9.4

Table 4.29: Concentrations (µg/g) of heavy metals in soil from Ikeja Industrial Estate.

Sample Code		**Lead**	**Cadmium**	**Zinc**	**Copper**	**Chromium**	**Nickel**
KBP-SL1	Mean	36±39	2.0±0.5	193±130	37±17	15±12	8.1±4
	Range	5-125	1.2-2.8	99-5110	23-72	6-48	2-17
KGI-SL2	Mean	100±70	2.0±1.4	335±44	70±44	24±21	12±8
	Range	30-217	0.3-47	249-422	22-176	4-65	5-27
KWS-SL3	Mean	40±21	1.3±0.6	181±78	26±2	17±4	9±3
	Range	11-75	0.5-2.3	99-321	22-30	8-23	6-14
KMB-SL4	Mean	29±8	3.0±1.3	414±180	28±11	16±7	8.2±4
	Range	21-42	0.7-5.1	221-767	17-43	9-29	3-15
K-SL	Mean	52±21	2.0±0.6	280±98	41±14	18±8	10±3
	Range	20-90	1.1-2.90	201-505	23-73	7-32	7-16
K-CTR-SL1	Mean	60±12	2.2±1.0	120±22	71±14	98±7	19±5
	Range	38-77	1.0-4.4	96-162	42-97	87-111	11-25
K-CTR-SL 2	Mean	58±10	2.0±0.3	114±20	70±14	99±7	18±3
	Range	39-70	1.1-2.2	97-166	44-99	90-109	14-22
K-CTR-SL	Mean	59±11	2.0±0.6	117±21	71±14	99±7	18±4
	Range	38-72	1.0-3.0	97-164	43-98	88-109	13-24

Zn ranging from 99-767 µg/g, with point KMB-EF having the highest mean level of 414±175 µg/g. The levels of clay were observed to be high for this soil and clay binds up metal because clay minerals are hydrous aluminium, magnesium or iron silicates. It therefore means that the metals are associated to the clay particles in the soil.

Cu ranged from 17-176 µg/g with point KGI-SL2 had the highest concentration of 70±44 µg/g. Cr and Ni ranged from 4-65 µg/g and 2-27 µg/g respectively with point KGI-SL2 had the highest concentration of 24±2 µg/g and 12±8 µg/g respectively.

The high concentration of Cr and Ni in point KGI-SL2 could be associated to the high level of % organic matter.

The control soil samples (K-CTR-SL) are higher in Pb, Cu, Cr and Ni when compared to the soil from Ikeja industrial estate (K-SL).

Generally, soil collected around KGI-SL2 (basic metal industry) had the highest concentrations of Pb, Cu, Cr and Ni while concentrations of Cd and Zn were highest in KMB-SL4 (pharmaceutical industry) sampling point.

The PCA diagram in Figure 4.26 shows KGI-SL2 with the highest concentrations of Pb, Zn, Cu, Ni and Cr. The corresponding analysis in Figure 4.27 shows the relative abundance of the metals which were in the order: Zn > Cd > Pb > Ni > Cu > Cr. The cluster analysis dendrogram in Figure 4.28 shows three clusters of KBP-SL1 and KWS-SL3, K-CTR-SL1 and K-CTR-SL2; and KGI-SL2 and KMB-SL4.

Table 4.30 shows the Pearson correlation coefficient results between parameters determined in soil around Ikeja industrial estate. There were low correlation between Pb and Cd (r=0.268); Pb and %organic matter (r = 0.311); Pb and Cu (r = 0.285); Zn and % Silt (r = 0.327) while negative low correlation existed between Ni and %organic matter (r = -0.289); at 95% confidence level. At 99% confidence level there were correlation between % organic matter and Zn; Cd and Ni.

From the analysis of variance at 95% confidence limit, there were significant difference in pH, %organic matter, %sand and clay, %silt, Pb, Zn, Cu, Cr and Ni between the sampling

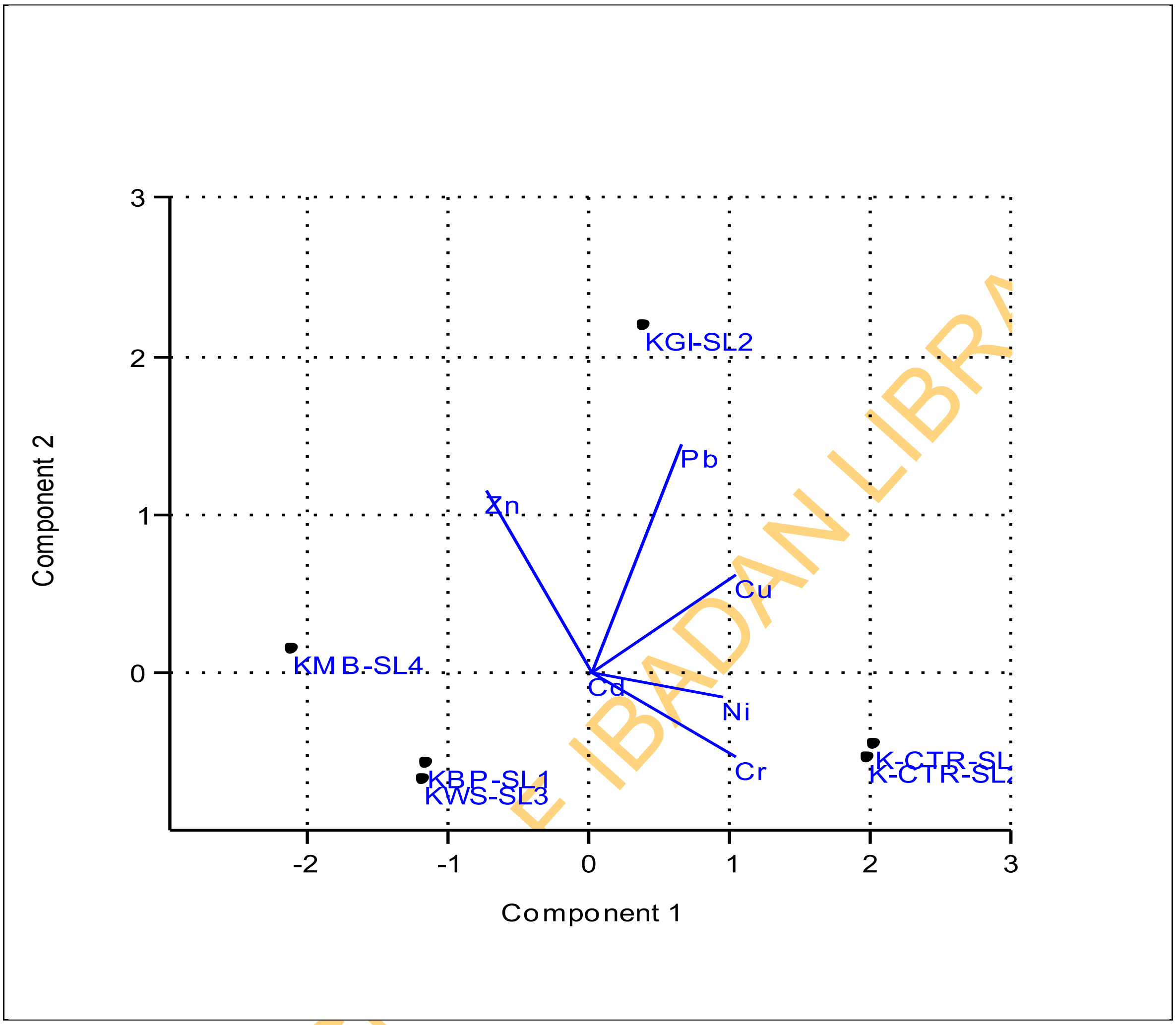

Fig 4.26: Principal component bi-plot of data on soil metals concentrations in Ikeja Industrial Estate.

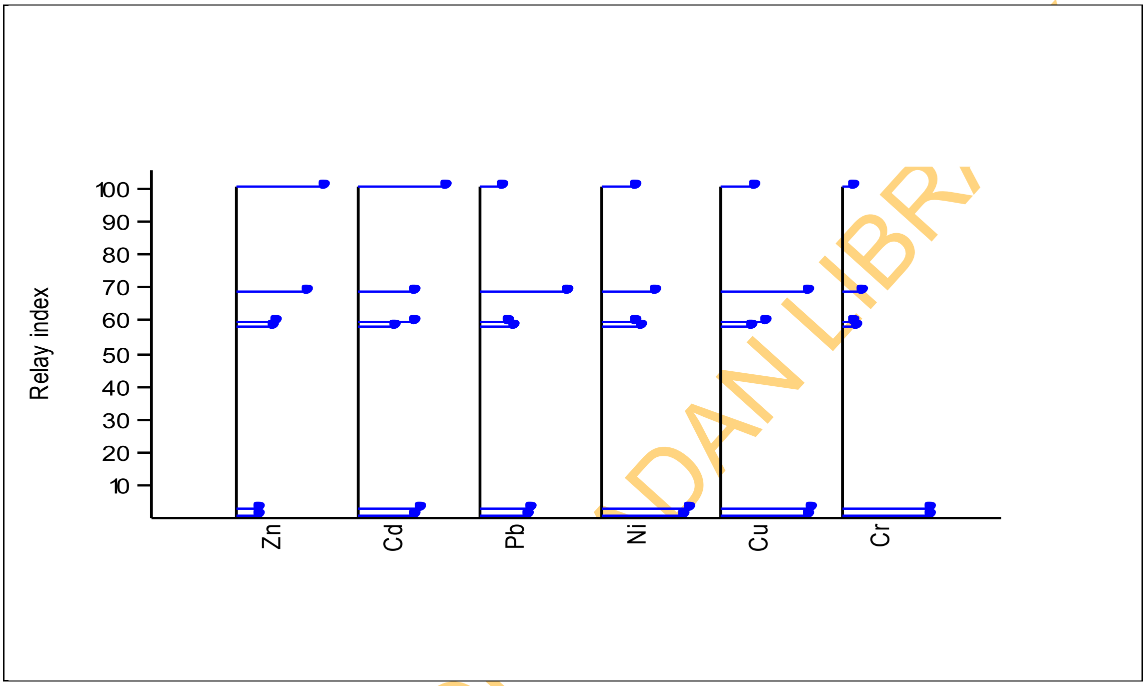

Fig 4.27: Corresponding analysis relay plot for six metals in Ikeja Industrial Estate.

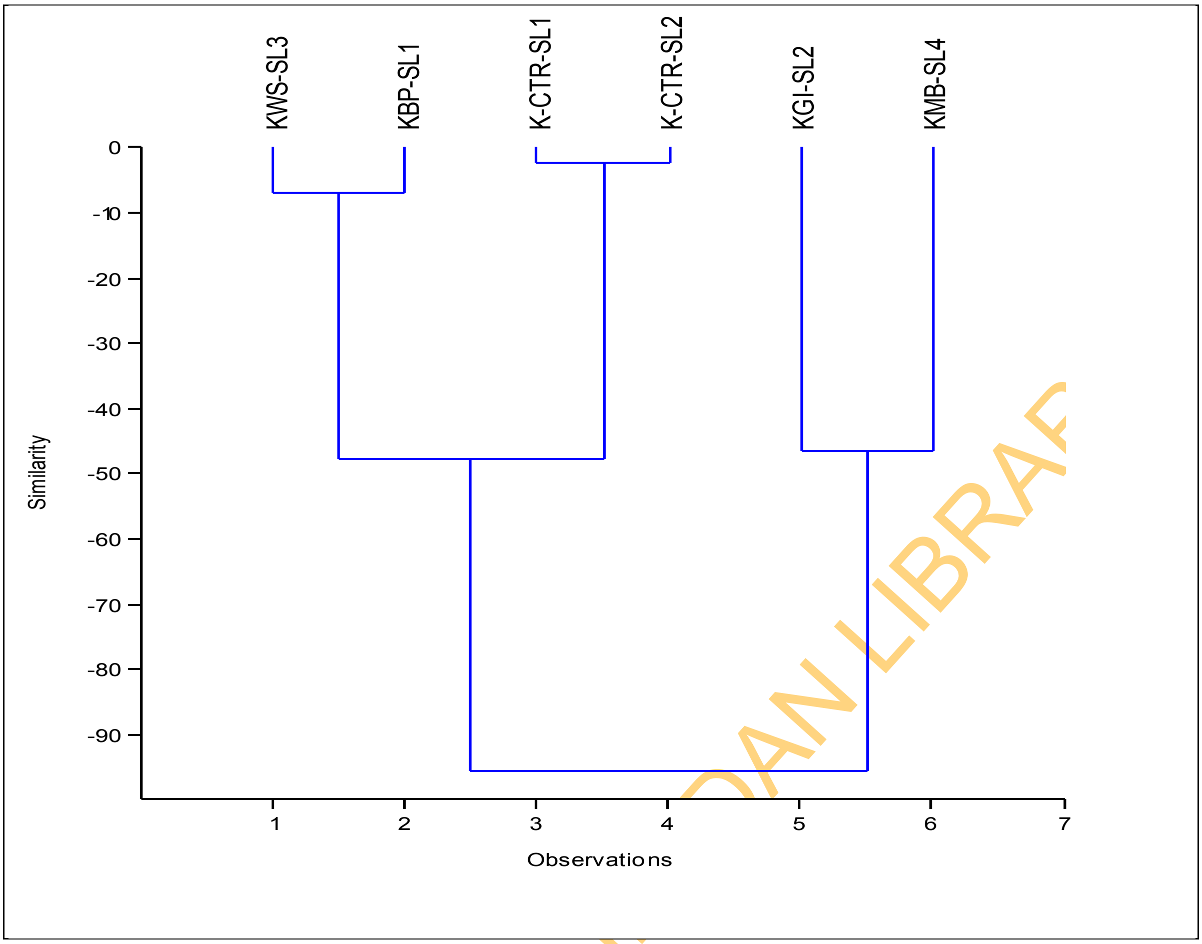

Fig 4.28: Cluster analysis dendrogram for soil using the metals concentrations in Ikeja Industrial Estate.

Table 4.30: Pearson correlation coefficients for metal contents of soil around Ikeja Industrial Estate.

	pH	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**	**% OC**	**% OM**	**% Sand**	**% Clay**	**% Silt**
pH	1											
Pb	-0.325[a]	1										
Cd	0.213	0.268[a]	1									
Zn	-0.084	0.191	0.033	1								
Cu	0.074	0.285[a]	0.082	-0.229	1							
Cr	0.409[b]	0.160	0.128	-0.534[b]	0.487[b]	1						
Ni	0.134	0.468[b]	0.420[b]	-0.355[b]	0.531[b]	0.692[b]	1					
% OC	-0.369[b]	0.312[a]	0.005	0.574[b]	-0.216	-0.580[b]	-0.289[a]	1				
% OM	-0.369[b]	0.311[a]	0.002	0.575[b]	-0.209	-0.576[b]	-0.289[a]	1.000[b]	1			
% Sand	-0.120	-0.050	-0.199	-0.206	-0.021	-0.074	-0.083	-0.162	-0.161	1		
% Clay	0.240	-0.155	0.019	-0.004	-0.077	0.183	0.013	-0.112	-0.114	-0.846[b]	1	
% Silt	0.006	0.193	0.289[a]	0.327[a]	0.085	-0.032	0.108	0.346[b]	0.346[b]	-0.918[b]	0.566[b]	1

[a] Significant at the 0.05 level.

[b] Significant at the 0.01 level.

points during the period of sample. Cd shows no significant difference between the sampling points.

Paired student t-test (95% confidence limit) showed no significant difference in Pb and Cd concentrations between soil from the ikeja industrial estate and the control soil while Zn, Cu, Cr and Ni concentrations showed a significant difference between the soil sample and the control soil.

4.8.2 Characteristics of Soil around Isolo Industrial Estate

The pH of soil in Isolo industrial estate ranged within 6.7-8.8 while the control pH ranged within 7.2-8.6. The soil pH was near neutral (Table 4.31). This was similar to the pH range obtained from Ikeja industrial estate soil. The % organic matter ranged from 0.5-5.7 while SJW-SL1 had the highest level of % organic carbon of 2.2±2.1 for all the months sampled. % sand ranged within 75.9-97.0 with point SAF-SL4 had the highest level of 94.1±1.9 for all the period of sampling. % clay and % silt ranged within 2.6-14.0 and 0.4-18.4 respectively with SJW-SL1 had the highest value of % clay 87.9±6.6 and % silt 4.6±5.9 for all the period of sampling.

Pb concentration in soil was found to be high compared to the control soil; this ranged within 3-65 µg/g with points SJW-SL3 and SAF-SL5 had high concentrations for all the period of sampling (Table 4.32).

Cd concentration ranged within 0.12-1.75 µg/g with point SJW-SL3 and SVJ-SL6 had high concentration of 0.82±0.48 µg/g and 0.76±0.54 µg/g respectively for all the period of sampling. The Cd concentration in the soil at SJW-SL3 are higher compared to the control soil, but the average Cd in the soil samples(S-SL) were lower than the average of the control(S-CTR-SL). There was no significant difference in Cd between the soil sample from the estate and the control sample.

Zn ranged within 13-135 µg/g with SJW-SL3 and SVJ-SL6 having the highest concentration of 57±22 µg/g and 56±40 µg/g respectively. The soil sample (S-SL) Zn average was lower than the average control (S-CTR-SL). There was no significant difference in Zn between the soil sample and the control sample.

Table 4.31: pH, organic matter and particle size characteristics of soil from from Isolo Industrial Estate.

Site Code		pH	Organic Carbon (%)	Organic Matter (%)	Sand (%)	Clay (%)	Silt (%)
SJW-SL1	Mean	7.9±0.8	1.3±1.2	2.2±2.1	87.9±6.6	7.5±4.0	4.6±5.9
	Range	7.0-9.1	0.3-3.3	0.5-5.7	75.9-96.0	3.6-14.0	0.4-18.4
SJW-SL2	Mean	7.8±0.8	0.7±0.4	1.2±0.7	92.7±4.1	5.1±1.8	2.2±2.7
	Range	7.1-9.1	0.4-1.5	0.6-2.7	81.9-95.0	3.6-8.4	0.2-9.7
SJW-SL3	Mean	7.5±0.8	1.2±0.5	2.2±0.9	92.4±1.5	5.1±0.9	2.4±1.5
	Range	6.4-8.5	0.4-2.0	0.9-3.4	90.9-96.0	3.6-6.2	0.4-4.5
SAF-SL4	Mean	7.7±08	0.7±0.3	1.2±0.4	94.1±1.9	4.7±1.5	1.3±0.7
	Range	6.6-8.8	0.4-1.2	0.8-2.1	92.2-97.0	2.6-7.2	0.4-2.4
SAF-SL5	Mean	7.9±0.8	1.3±1.1	2.2±1.8	93.4±1.4	5.1±0.8	1.3±0.6
	Range	6.6-8.9	0.4-3.2	0.6-5.5	91.9-96.0	3.6-5.8	0.4-2.5
SVJ-SL6	Mean	7.4±0.9	1.3±0.7	2.2±1.2	92.3±3.2	4.4±1.2	3.3±3.5
	Range	6.5-8.7	0.6-2.8	1.0-4.9	86.6-95.7	2.6-5.9	0.6-9.8
S-SL	Mean	7.7±0.7	1.1±0.4	1.9±0.6	92.1±1.6	5.3±1.2	2.5±1.0
	Range	6.7-8.8	0.6-1.6	1.1-2.8	89.6-94.2	3.8-7.8	1.4-4.7
S-CTR-SL1	Mean	7.6±0.5	0.5±0.1	0.9±0.2	85.2±4.6	7.1±2.4	7.7±3.1
	Range	7.2-8.6	0.3-0.7	0.5-1.2	76.0-90.1	4.6-12.3	3.4-11.7
S-CTR-SL2	Mean	7.8±0.4	0.5±0.1	0.9±0.2	87.6±1.8	5.2±0.8	7.2±1.3
	Range	7.3-8.3	0.3-0.8	0.6-1.4	85.5-90.7	3.8-6.4	5.4-9.4
S-CTR-SL	Mean	7.7±0.2	0.5±0.1	0.9±0.2	86.4±3.0	6.2±1.3	7.5±1.9
	Range	7.4-8.0	0.4-0.7	0.6-1.2	80.7-90.3	4.2-8.7	5.0-10.6

Table 4.32: Concentration of metals (µg/g) of soil from Isolo Industrial Estate.

Site Code		**Lead**	**Cadmium**	**Zinc**	**Copper**	**Chromium**	**Nickel**
SJW-SL1	Mean	18±7	0.49±0.43	42±24	15±7	5.9±2.2	4.9±2.4
	Range	12-32	0.12-1.37	13-76	7-33	3.0-9.0	2.1-9.3
SJW-SL2	Mean	14±6	0.72±0.42	49±21	17±13	5.1±3.1	6.0±3.1
	Range	3-21	0.32-1.70	30-96	1-43	2.2-10.1	1.3-11.9
SJW-SL3	Mean	26±11	0.82±0.48	57±22	41±56	8.4±3.7	7.5±3.3
	Range	15-44	0.16-1.52	35-96	11-195	3.9-16.4	2.8-11.3
SAF-SL4	Mean	20±6	0.66±0.33	45±20	11.4±3	5.9±1.7	5.6±2.8
	Range	13-29	0.30-1.10	21-79	7-15	2.6-6.6	1.9-11.3
SAF-SL5	Mean	20±11	0.61±0.31	46±25	21±20	6.0±2.0	4.6±2.3
	Range	10-40	0.20-1.13	23-85	6-76	1.7-8.2	1.7-8.8
SVJ-SL6	Mean	28±20	0.76±0.54	59±40	40±14	7.8±1.9	5.3±2.3
	Range	13-65	0.17-1.75	33-135	13-64	4.9-9.5	2.4-8.6
S-SL	Mean	21±8	0.68±0.33	50±22	24±15	6.5±1.3	5.6±1.7
	Range	13-33	0.36-1.29	30-86	14-66	4.2-8.0	2.8-8.2
S-CTR-SL1	Mean	2±1	0.67±0.40	58±16	23±5	9.5±2.7	7.7±2.4
	Range	1-3	0.32-1.53	30-82	15-31	6.8-14.0	5.2-12.5
S-CTR-SL2	Mean	3±1	0.95±0.33	58±11	21±2	8.4±0.5	8.7±2.4
	Range	1-4	0.54-1.65	43-78	17-25	7.7-9.4	6.3-13.2
S-CTR-SL	Mean	3±1	0.81±0.23	58±11	22±3	8.9±1.4	8.2±1.5
	Range	1-3	0.54-1.15	44-80	16-26	7.2-11.1	6.2-11.1

Cu concentration was highest in points SJW-SL3 and SVJ-SL6 with average concentration of 41±56 µg/g and 40±14 µg/g respectively. The concentration of Cu in the soil sample was higher than the concentration in the control sample. There was no significant difference in Cu between the soil sample and the control sample.

Cr concentration ranged from 1.7-16.4µg/g with points SJW-SL3 and SVJ-SL6 had the highest concentration. The average Cr concentration in SJW-SL3 and SVJ-SL6 are 8.4±3.7 µg/g and 7.8±1.9µg/g respectively. Ni concentration ranged within 1.3-11.9 µg/g with point SJW-SL3 having the highest concentration of 7.5±3.3 µg/g.

Paired student t-test showed significant difference in Cr and Ni concentrations between sample soils and control soil at 95% confidence level.

Generally, sampling points SJW-SL3 and SVJ-SL6 had the highest concentrations of the metals analysed as shown in the PCA diagram in Figure 4.29. The cluster analysis dendrogram in Figure 4.30 shows three clusters for the sampling points which are in line with the PCA deduction The corresponding analysis in Figure 4.31 shows the relative abundance of the metals. This shows the relative abundances are in order of Ni > Cr >Zn > Cd > Cu > Pb.

Table 4.33 shows the Pearson correlation coefficient results between the parameters determined in soil around Isolo industrial estate. There are low correlation between Ni and % sand (r = -0.258); % organic matter and % clay(r = 0.286) at 95% confidence level. At 99% confidence level there are low correlation between % organic matter and Pb (r = 0.335); Cd and Ni (r = 0.293).

Analysis of variance at 95% confidence limit showed significant difference for Pb, Cu, Ni, %organic matter, %sand, %clay and %silt between the sampling points. pH, Cd, Zn and Cr showed no significant difference between sampling points during the period of sampling.

Paired student t-test (95% confidence limit) showed significant difference in Pb, Cr and Ni concentration between soil from Isolo Industrial Estate and the control. Cd, Zn, and Cu concentration did not show any significant difference between sample soil and the control soil.

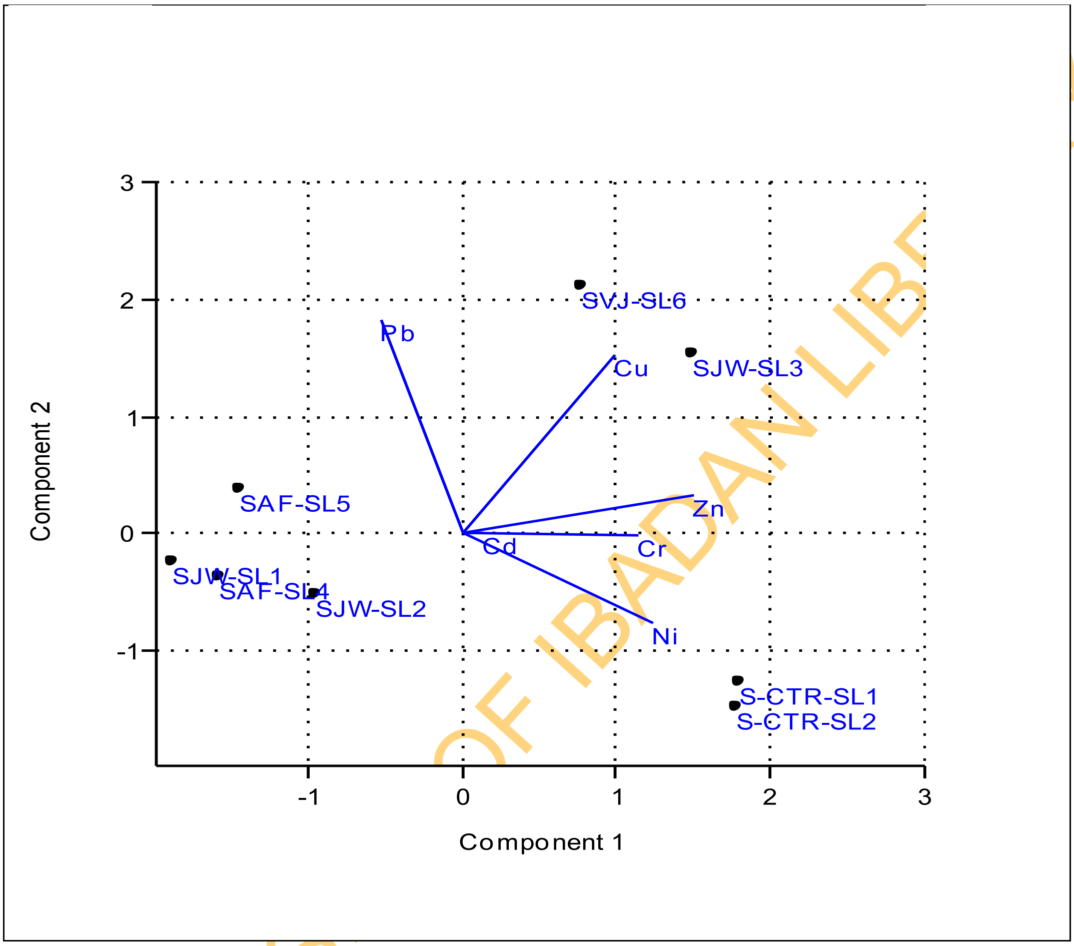

Fig 4.29: Principal Component bi-plot of data on soil metals concentrations in Isolo Industrial Estate.

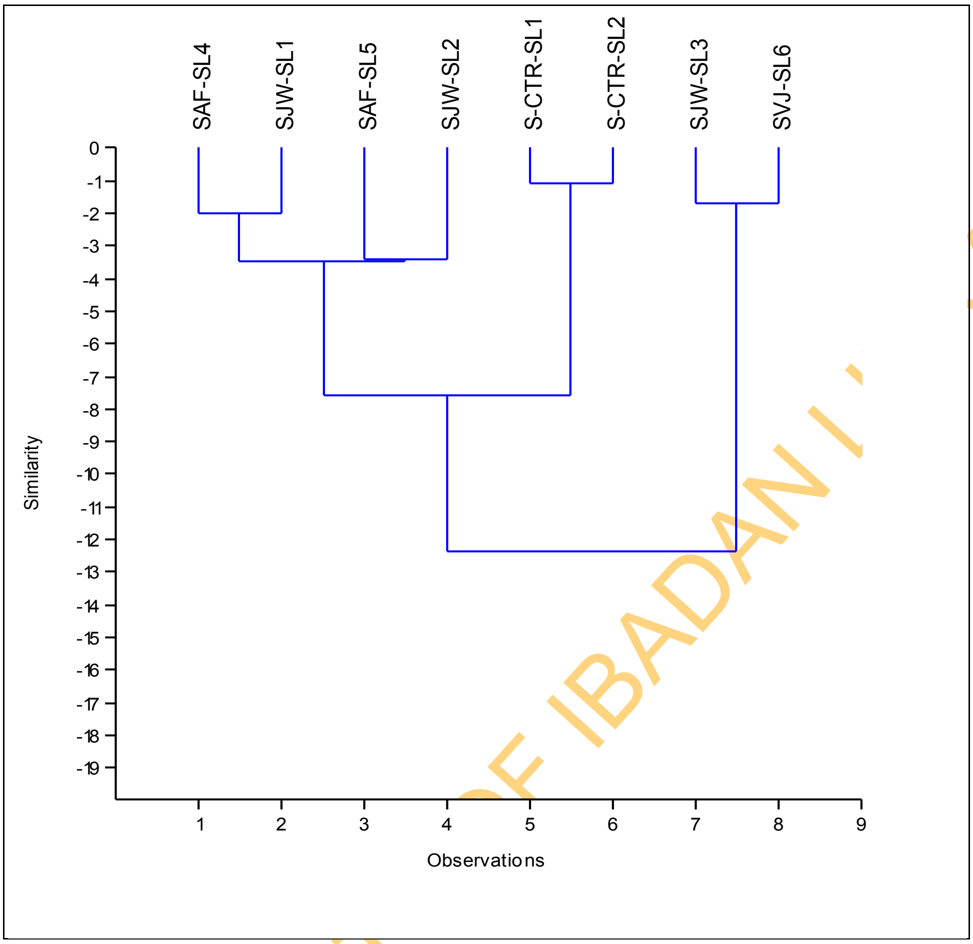

Fig 4.30: Cluster analysis dendrogram of data on soil metals in Isolo Industrial Estate.

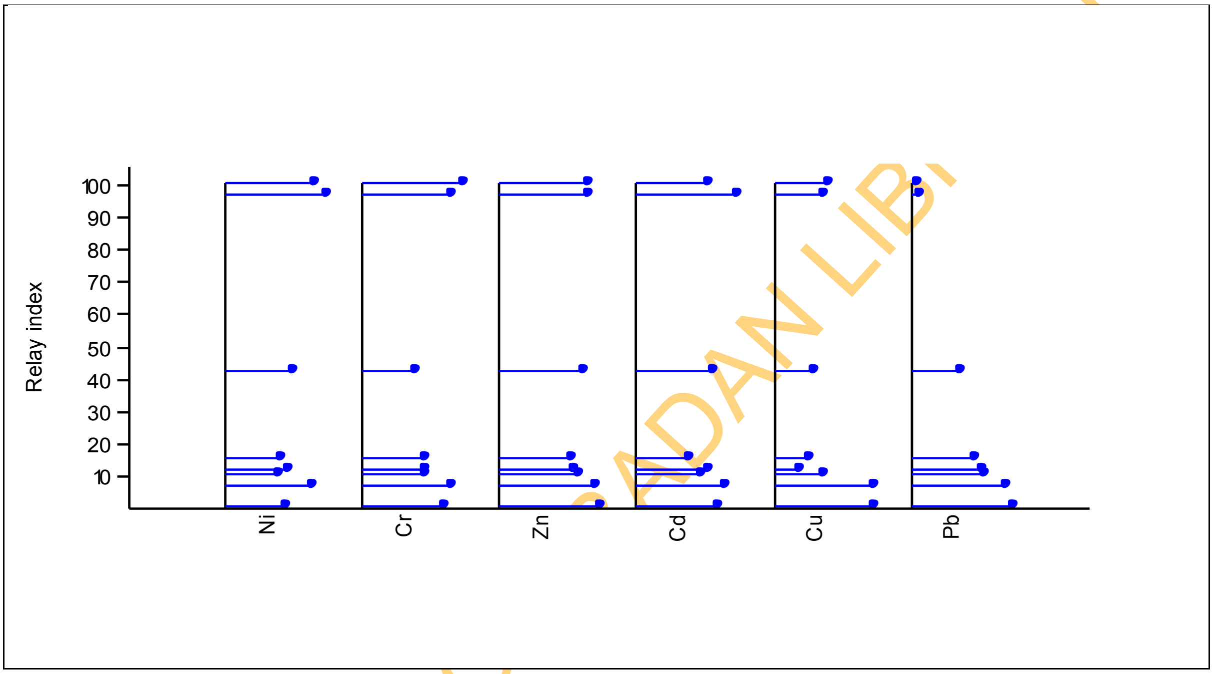

Fig 4.31: Correspondence analysis relay plot for heavy metals in Isolo Industrial Estate.

Table 4.33: Pearson correlation coefficient for metal contents of soil around Isolo Industrial |Estate.

	pH	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**	**% OC**	**% OM**	**% Sand**	**% Clay**	**% Silt**
pH	1											
Pb	-0.204	1										
Cd	0.396[b]	-0.186	1									
Zn	-0.320[b]	0.492[b]	-0.114	1								
Cu	-0.052	0.190	0.173	-0.045	1							
Cr	-0.192	-0.028	0.182	0.047	-0.050	1						
Ni	-0.117	0.055	0.293[b]	0.477[b]	0.138	0.120	1					
% OC	-0.122	0.335[b]	0.102	0.013	0.216	-0.008	0.015	1				
% OM	-0.122	0.335[b]	0.102	0.013	0.216	-0.008	0.015	1.000[b]	1			
% Sand	0.003	0.337[b]	-0.095	-0.038	-0.038	-0.026	-0.258[a]	-0.123	-0.123	1		
% Clay	0.033	-0.175	-0.004	-0.035	-0.057	-0.020	-0.022	0.286[a]	0.286[a]	-0.635[b]	1	
% Silt	-0.020	-0.327[b]	0.125	0.064	0.082	0.046	0.335[b]	-0.013	-0.013	-0.892[b]	0.218	1

[a] Significant at the 0.05 level.

[b] Significant at the 0.01 level.

4.9: COMPARISON OF HEAVY METALS IN SOILS STUDIED WITH SOIL QUALITY GUIDELINES

Metal levels in the study were compared with the soils from industrial and commercial areas criteria for Canada, Hong kong, Netherland, Norway and Switzerland (Table 4.34).The average Pb, Cd and Zinc in soil from Ikeja industrial estate (this study) exceeded the Norwegian and Swiss guides while the metal levels in Isolo industrial estate soil (this study) were lower than the above guides. The averages Cu, Cr, and Ni in the soils from both studies were below the guidlelines of Canada, Hong Kong, Netherland, Norway and Switzerland.

Cd and Zn were established as metals of significant environmental concern at Ikeja industrial estate soil compared with Isolo industrial estate soil. Levels of Cu, Cr, and Ni did not reveal appreciable contamination from the activities around the industrial estate. This could have a link to the geological formation of soil in this area. (Zupan *et al.*, 2000).

4.10: EFFECT OF SEASONAL VARIATION ON THE SOIL QUALITY

4.10.1: pH and % Organic matter

The pH of the Ikeja and Isolo industrial estate soil were generally near basic for both estate while the control for both estate were near basic too as shown in Table 4.35a and Table 4.36a respectively. There were no clear seasonal variations for soil pH as shown from the monthly variation in pH values in Figure 4.32. Soils generally had pH values within the range of 4.0 – 8.5, due to buffering by Al^{3+} at the lower end and $CaC0_3$ at the upper end of the range (Wild, 1998). Generally, soils have several mechanisms which serve to buffer pH to varying exchange reactions. Since soils are affected by change on redox potential which occurs in most tropical soils, the pH range recorded in these soils indicate oxidizing conditions. Heavy metals are most mobile and bioavailable under acidic conditions. The bioavailability of heavy metal ions in soil is influential by many factors. The most important factor affecting metal availability is soil pH (Tordoff *et al.*, 2000; Jordan *et al.*, 2002). Brady (1984) stated that the normal pH is 5 – 7 in soils of humid regions and 7-9 in soils of arid regions. The optimal pH for most arable crops is 6.5 on mineral soils and 5.5 on peaty soil which means that the upper most layer of the regolith does support crop production and vegetation favourably. The percentage organic matter ranged within 1.3 – 7.4 and 1.1 – 2.8 for Ikeja and Isolo Industrial Estate respectively as shown in Table 4.35a and Table 4.36a while the controls respectively ranged within 1.1 – 2.5 and 0.6 – 1.2. The seasonal variations in % organic matter are shown in Figure 4.33

Table 4.34: Soil quality criteria for some countries compared with level (µg/g) obtained from this study.

Country Definition		**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**	**Reference**
Ikeja, Nigeria (This study)	Mean	52± 21	2.0 ± 0.6	208 ± 98	41 ± 14	18 ± 8	10 ± 3	This study
	Range	20 – 90	1.1 – 2.90	201 – 505	23 – 73	7 – 32	7 – 16	This study
Isolo, Nigeria (This study)	Mean	21 ± 8	0.68 ± 0.33	50 ± 22	24 ± 15	6.5 ± 1.3	5.6 ± 1.7	This study
	Range	13 – 33	0.36 – 1.29	30 – 86	14 – 66	4.2 – 80	2.8 – 8.2	This study
Norway		50	1.0	150	100	100	30	Reimann *et al.* (1997)
Netherland	action level	530	12	720	190	380	210	Reimann *et al.* (1997)
Switzerland	Guide Value	50	0.8	200	50	-	-	FOEFL (1987)
Canada	Industrial	600	22	360	91	87	50	CCME (1999)
Canada	Commercial	260	22	360	91	87	50	CCME (1999)
Hong Kong		90	0.9	59	16	-	-	Chen *et al.* (1997)

Table 4.35a: Average seasonal physicochemical quality of soil from Ikeja Industrial Estate.

	Wet Season						Dry Season					
Site Code	pH	% OC	% OM	% Sand	% Clay	% Silt	pH	% OC	% OM	% Sand	% Clay	% Silt
KBP-SL1	6.5±0.2	1.8±1.6	3.1±2.8	95.3±1.7	2.9±0.6	1.9±1.4	6.4±0.5	1.7±1.4	2.9±2.5	94.0±2.2	3.3±0.9	2.9±1.5
KGI-SL2	6.3±0.5	3.0±0.9	5.2±1.5	91.6±1.5	2.4±0.5	6.0±1.9	6.2±0.7	3.2±1.3	5.6±2.2	90.7±3.0	2.8±1.1	6.6±2.7
KWS-SL^{-}	6.5±0.6	2.1±0.5	3.6±0.8	89.9±5.3	4.9±2.9	5.2±2.5	6.5±0.8	2.6±0.9	4.4±1.6	89.5±4.1	5.2±2.1	5.3±2.1
KMB-SL4	7.6±0.2	3.0±1.2	5.1±2.1	87.7±9.6	4.9±3.5	7.7±6.7	7.5±0.4	2.2±1.0	3.7±1.8	86.1±7.1	6.5±3.3	7.4±4.0
K-SL	7.7±0.7	2.7±1.0	4.7±1.8	98.5±14.1	4.2±2.0	5.7±3.3	6.9±0.6	2.4±0.9	4.2±1.5	90.1±3.6	4.4±1.4	5.5±2.2
K-CTR-SL1	7.3±0.4	0.7±0.1	1.1±0.2	88.1±5.6	6.9±3.4	5.0±2.4	7.4±0.6	1.2±0.3	2.0±0.5	89.3±3.8	4.5±1.3	6.2±2.9
K-CTR-SL2	7.3±0.3	0.8±0.2	1.5±0.3	90.5±3.2	5.8±2.0	3.7±1.7	7.3±0.6	1.1±0.2	1.9±0.3	90.2±3.9	4.2±1.4	5.6±2.8
K-CTR-SL	7.3±0.4	0.8±0.1	1.3±0.2	89.3±4.2	6.4±2.7	4.4±1.8	7.3±0.6	1.1±0.2	2.0±0.4	89.7±3.8	4.4±1.3	5.9±2.8

Table 4.35b: Seasonal concentration (µg/g) of metals in soil from Ikeja Industrial Estate.

	Wet Season						Dry Season					
Site Code	Lead	Cadmium	Zinc	Copper	Chromium	Nickel	Lead	Cadmium	Zinc	Copper	Chromium	Nickel
KBP-SL1	18±15	1.7±0.5	119±15	42±17	21±19	8±7	47±46	1.9±0.6	242±155	34±19	11±4	8±2
KGI-SL2	73±49	1.0±0.5	334±13	91±59	21±20	9±4	117±80	2.1±1.7	335±58	55±27	26±24	14±9
KWS-SL^{-}	37±14	1.5±0.5	131±29	27±2	17±2	10±3	42±26	1.1±0.7	214±84	24±1	17±5	9±3
KMB-SL4	35±8	3.0±1.9	329±113	35±11	15±9	8±5	26±6	2.2±0.7	470±194	23±8	16±6	8±4
K-SL	43±14	1.9±0.5	239±26	52±14	19±9	9±2	58±23	1.8±0.8	307±121	34±9	18±9	10±4
K-CTR-SL1	54±15	1.8±0.8	117±5	67±17	101±3	16±5	64±9	2.5±1.0	122±29	74±13	96±9	20±5
K-CTR-SL2	54±12	1.7±0.4	110±2	65±14	102±7	17±3	61±9	1.7±0.3	117±27	74±14	97±8	19±3
K-CTR-SL	54±14	1.8±0.6	113±3	66±15	101±5	17±4	62±9	2.1±0.6	119±27	74±13	97±8	20±4

Table 4.36a: Average seasonal physicochemical quality of soil from Isolo Industrial Estate.

	Wet Season						Dry Season					
Site Code	pH	% OC	% OM	% Sand	% Clay	% Silt	pH	% OC	% OM	% Sand	% Clay	% Silt
SJW-SL1	7.8±0.6	1.7±1.4	2.9±2.4	84.0±7.5	8.1±4.2	7.9±8.0	8.0±0.9	1.0±1.2	1.7±2.4	90.5±5.0	7.0±4.1	2.4±3.0
SJW-SL2	7.8±0.8	0.5±0.2	0.9±0.3	94.2±0.5	4.4±0.5	1.4±0.0	7.9±0.9	0.8±0.5	1.4±0.8	91.8±5.2	5.6±22	2.7±3.5
SJW-SL^{-}	7.0±0.7	1.7±0.3	2.9±0.4	92.8±2.2	4.4±1.0	2.8±2.0	7.8±0.7	1.0±0.4	1.7±0.7	92.2±0.8	5.6±0.5	2.2±1.2
SAF-SL4	7.7±0.9	0.7±0.2	1.2±0.4	93.7±1.6	4.7±1.2	1.6±0.8	8.1±0.7	0.7±0.3	1.2±0.5	94.3±2.1	4.7±1.8	1.0±0.6
SAF-SL5	7.0±1.1	1.3±1.3	2.3±2.2	93.2±0.2	5.5±0.1	1.4±0.0	8.0±0.9	1.3±1.0	2.2±1.8	93.6±1.9	4.9±1.0	1.3±0.8
SVJ-SL6	7.1±0.9	0.8±0.1	1.4±0.2	94.5±1.6	3.9±1.5	3.9±1.5	7.7±0.7	1.6±0.8	2.7±1.3	90.9±3.3	4.7±0.9	4.4±4.2
S-SL	7.4±0.7	1.1±0.4	1.9±0.7	92.1±1.7	5.2±0.5	2.8±1.4	7.9±0.8	1.0±0.4	1.8±0.6	92.2±1.7	5.4±1.6	2.3±0.6
S-CTR-SL1	7.6±0.6	0.5±0.1	0.9±0.1	87.0±4.6	7.3±1.8	5.7±3.4	7.6±0.5	0.5±0.1	0.9±0.2	83.9±4.5	7.0±2.9	9.1±2.1
S-CTR-SL2	7.9±0.4	0.6±0.1	1.0±0.3	87.5±1.9	5.2±0.8	7.4±1.3	7.8±0.4	0.5±0.1	0.9±0.2	87.6±1.9	5.2±0.8	7.2±1.4
S-CTR-SL	7.7±0.1	0.5±0.1	0.9±0.2	87.3±3.1	6.2±1.2	6.5±2.0	7.7±0.2	0.5±0.1	0.9±0.2	85.8±0.5	6.1±1.5	8.1±1.7

Table 4.36b: Seasonal concentration (µg/g) of metals in soil from Isolo Industrial Estate.

	Wet Season						Dry Season					
Site Code	Lead	Cadmium	Zinc	Copper	Chromium	Nickel	Lead	Cadmium	Zinc	Copper	Chromium	Nickel
SJW-SL1	18±9	0.39±0.47	33±4	17±1	5±3	4±2	18±6	0.56±0.44	48±30	14±10	6±2	5±3
SJW-SL2	11±4	0.86±0.13	35±4	20±17	3±1	4±3	16±7	0.63±0.53	58±23	15±12	7±3	7±3
SJW-SL^{-}	24±7	0.72±0.54	39±4	74±83	9±5	9±3	28±13	0.89±0.48	68±21	19±7	6±3	6±3
SAF-SL4	21±8	0.63±0.30	37±2	13±4	5±2	5±4	19±6	0.69±0.37	50±26	11±3	6±2	6±2
SAF-SL5	14±5	0.47±0.18	32±3	34±28	4±2	3±1	25±12	0.71±0.35	56±30	12±5	7±1	6±2
SVJ-SL6	22±9	0.57±0.46	38±6	46±8	6±2	3±1	33±25	0.88±0.59	74±48	36±17	9±1	7±2
S-SL	18±6	0.61±0.26	36±1	34±21	5±1	5±2	23±10	0.73±0.39	59±25	18±4	7±1	6±2
S-CTR-SL1	2±1	0.67±0.41	64±20	21±2	9±3	7±3	2±0.5	0.66±0.43	54±13	24±6	10±3	8±3
S-CTR-SL2	3±1	0.80±0.21	67±12	21±2	8±0.4	9±3	3±0.3	1.04±0.37	52±5	20±3	9±1	9±2
S-CTR-SL	2±1	0.74±0.21	66±14	21±2	9±2	8±2	3±0.3	0.85±0.25	53±7	22±4	9±1	8±2

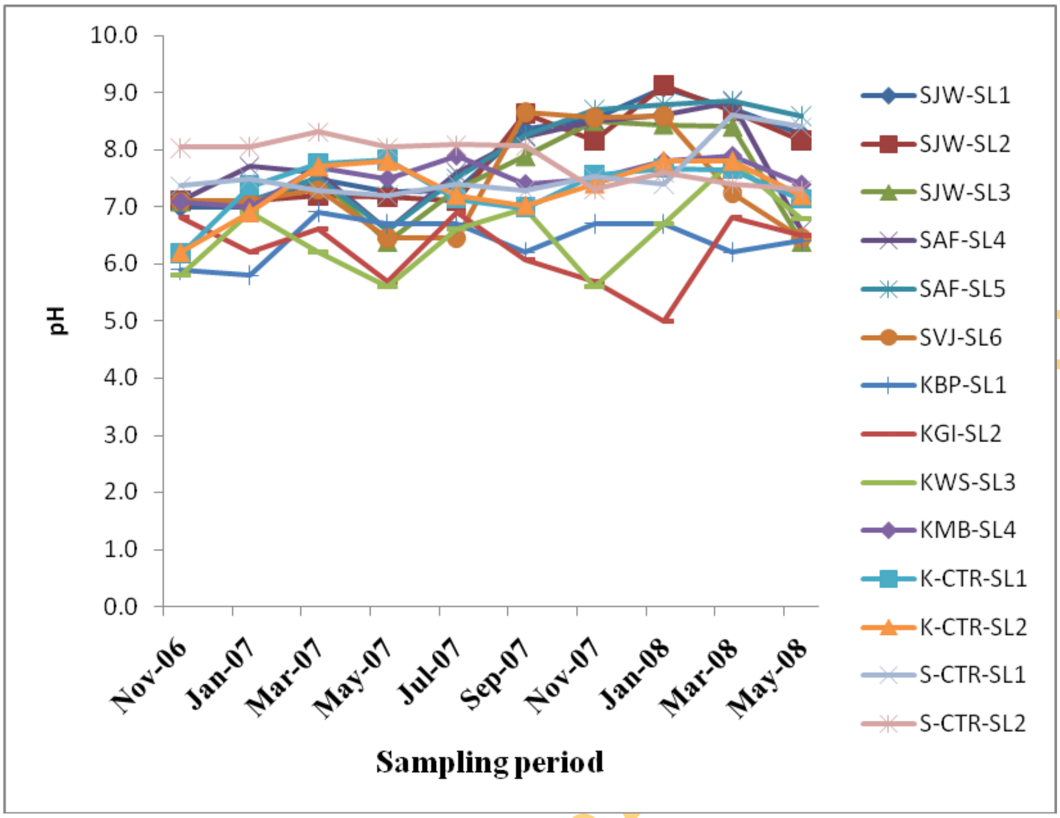

Fig. 4.32: Variations of pH of soils with sampling period.

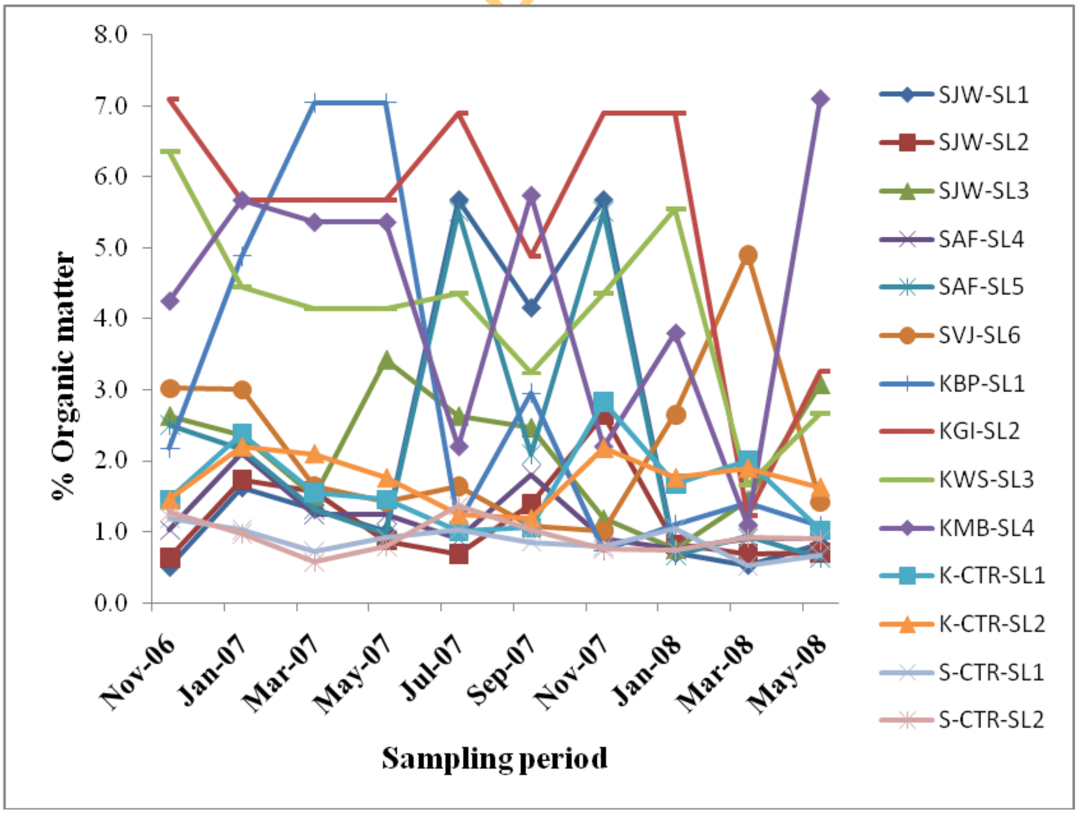

Fig. 4.33: Variations of soil organic matter content with sampling period.

The values of % OM as shown in Tables 4.35a and 4.36a for Ikeja and Isolo wet season value are 4.7±1.5 and 1.9±0.7 respectively while the dry season values are 4.2 ± 1.5 and 1.8 ± 0.6. Alloway, (1990) stated that the higher the organic matter content, the more it absorbs heavy metals. This may indicates that organic matter may play a significant role in the absorption of these metals in soils from the different locations of the study area. Organic matter content plays an important role in the soil structure, water retention and in the formation of complexes (Alloway and Ayres, 1997).

pH and organic matter content of the soil were not significantly different from one season to another.

4.10.2 Soil Particle Size Characteristics

Tables 4.35a and 4.36a gave the percentage sand, clay and silt content of the soil within the study area for Ikeja and Isolo industrial area respectively. The wet season % sand and silt values were: 98.5 ± 14.1 and 5.7 ± 3.3; 92.1 ± 1.7 and 2.8 ± 1.4 respectively. The dry season values were 90.1 ± 3.6 and 5.5 ± 2.2; 92.2 ±1.7 and 2.3 ± 0.6 respectively. T-test (95% confidence level) showed no significant different between the wet seasons and dry season for the soil samples and the control sites.

4.10.3 Lead

Pb concentrations obtained are shown in Tables 4.29 and 4.32 for Ikeja and Isolo Industrial area respectively. The Pb concentrations in soil samples from Ikeja industrial area (52 ± 21 µg/g) which are lower than the control site (59 ± 11µg/g), there was no significant difference between the values. The Industrial activities within Ikeja industrial estate had no significant effect on the soil within the estate. Isolo industrial area Pb concentrations were higher in the soil samples (21±8 µg/g) than the control site (3±1 µg/g). There was significant difference between the values. This shows that the activity of the industries within the Isolo industrial estate had a significant impact on the soil within the estate. Accumulation factors were calculated by dividing each metal level in different sites by levels in control. Accumulation factor for Pb in the soil from Ikeja industrial estate and Isolo Industrial Estate are 0.9 and 9.0 respectively. Thus, Isolo Industrial Estate soil had significant contamination of Pb in the top soil.

Lead concentration showed seasonal variation with the dry season having the highest levels for all sample sites (Table 4.35b and 4.36b). The monthly variations in Figure 4.34 showed increased concentration of Pb during the months of January 2007 and November 2007. This invariably was the dry months of the year which explains the elevated levels of Pb. During these months, the Pb only accumulates in the soil either through atmospheric deposition, effluent discharge or evacuation of sediments unto Land, in contrast to the wet months of March 2007, May 2007, July 2007 and September 2007 in which precipitation leaches particulate Pb from the top soil, thereby reducing it concentration.

Level of Pb (52 ± 21 µg/g) and (21 ± 8 µg/g) in Ikeja and Isolo industrial areas respectively are lower than that obtained in top soils (81 µg/g) in Ibadan Nigeria (Onianwa *et al*., 2001), around Auto workshops (805 µg/g), gas stations (392 µg/g) and motor parks (266 µg/g) in Ibadan city (Onianwa *et al*., 2001).

4.10.4 Cadmium

Cd concentrations for Ikeja and Isolo industrial estates are 2.0±0.6 µg/g and 0.68±0.33 µg/g respectively as shown in Tables 4.29 and 4.32. The Cd concentrations of Ikeja and Isolo soil compared to the control showed no significance difference. There were no seasonal variations (Table 4.35b and 4.36b) for Ikeja and Isolo industrial estate soils respectively in Cd levels. The accumulation factors of cadmium in the soil were Ikeja soil – 0.8 and Isolo – 1.0 respectively. These reflect relatively low Cd levels in the estates soils. The average concentration of Cd in the earth's crust is above 0.1 µg/g (Alloway,1997). Cd content of soil was determined by the chemical composition of the parent rock. The content varies between 0.1 –0.3 µg/g in igneous rocks and 3–11 µg/g in sedimentary rocks (Pager *et al*., 1987). The average content of Cd in unpolluted soil lies between 0.07 and 1.1µg/g. Generally, most soils can be expected to contain <1µg/g Cd except those contaminated from discrete sources or development in parent materials with anomalously high Cd contents, such as black shales. The monthly variation in Figure 4.35 shows no spatial variation in concentration of Cd in the soils sample. Cd levels in soils around Isolo industrial area are 0.68±0.33 µg/g and the control $0.81^{\pm}0.23$ µg/g were relatively close to global background concentrations hence may not be considered contaminated with Cd.

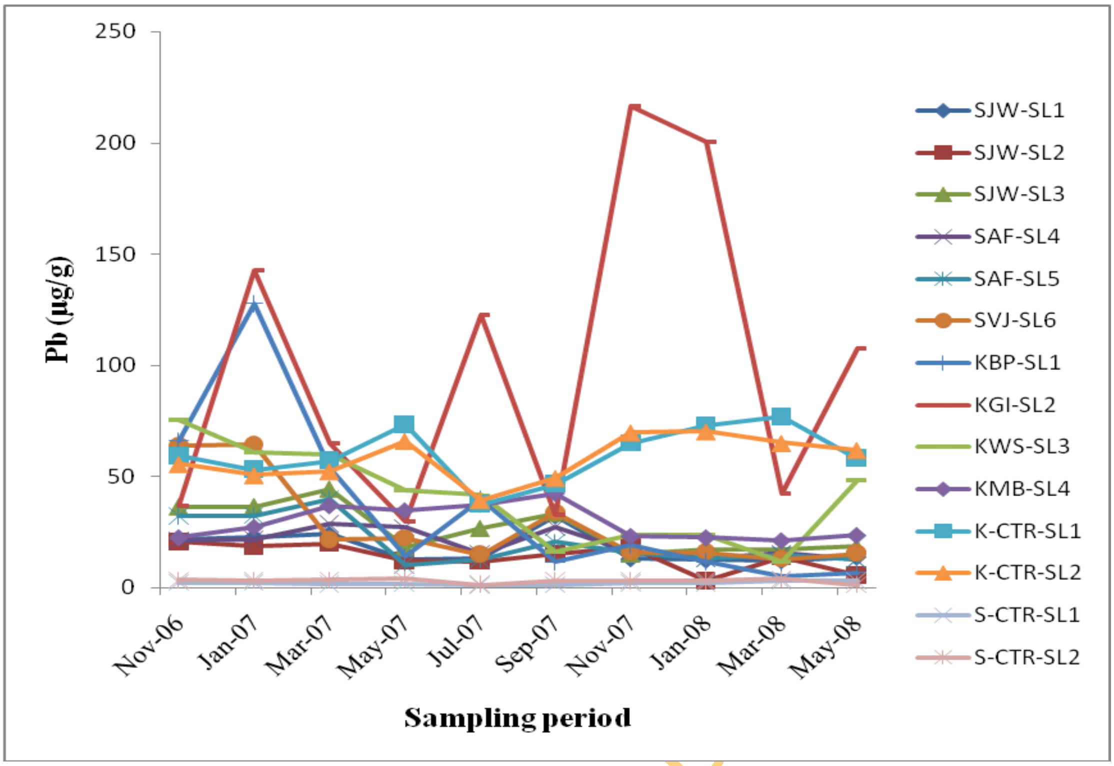

Fig. 4.34: Variations of lead contents of soils with sampling period.

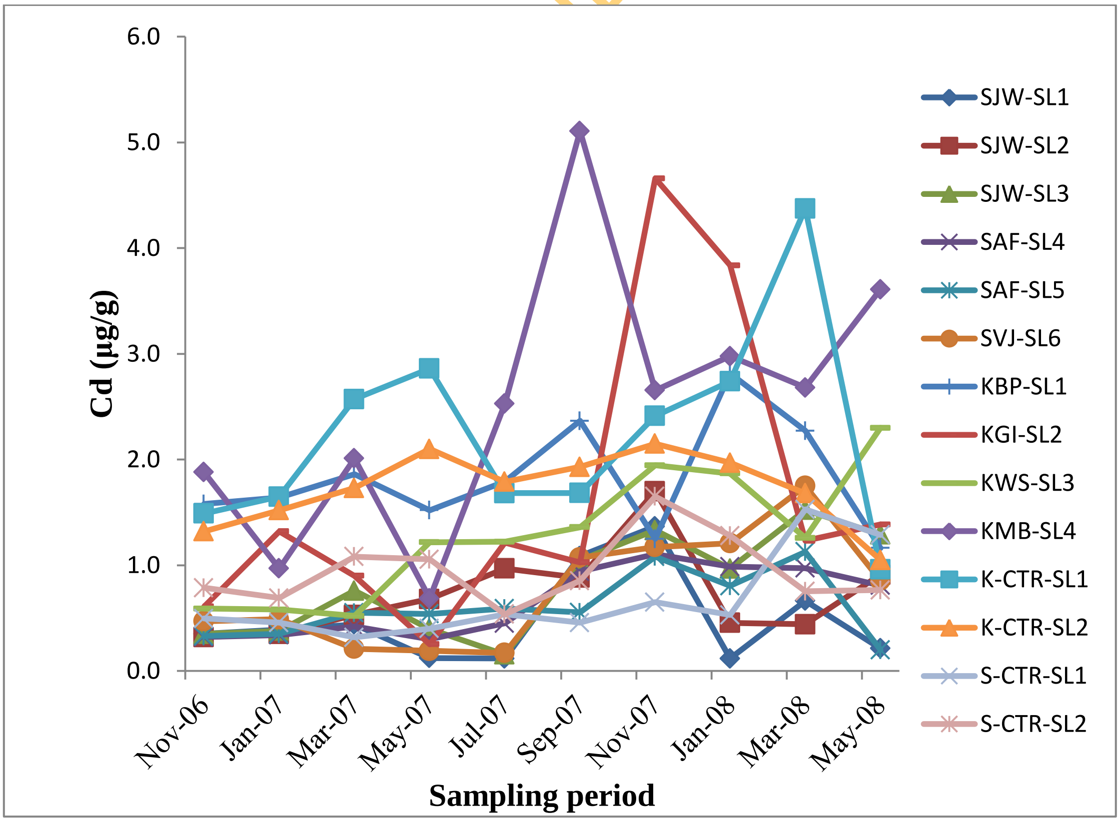

Fig. 4.35: Variations of cadmium contents of soils with sampling period.

Ikeja industrial area soil Cd concentrations are 2.0±0.6 µg/g and the control 2.0±0.6 µg/g was higher than the global background concentration. In the USA, a survey of soils from uncontaminated sites revealed a range of Cd contents from 0.005 to 2.4 µg/g, while in England and Wales Cd content of 1.2µg/g was reported. However, the background Cd level in soils apparently should not exceed 0.5 µg/g (0.07–1.1 µg/g). Values higher than the background Cd levels reflect anthropogenic impact.

It was observed that the Cd in soil increases with Zn content and these elements are much higher in surface soil (0 – 15cm) than sub surface soil (15 – 60cm) (Jarup *et al*., 1998), though Cd tend to move down the profile more readily than Pb or Cu. Biddappa *et al*. (1982) found that Cd, Ni and Zn were readily leached down columns of two Japanese soils than Cu and Pb are thus constitute a greater ground water pollution risk. Cadmium is most mobile in acidic soils within the range of pH 4.5–5.5, which means that Cd was not expected to be of environmental significance with the studied area.

Levels of Cd (2.0 µg/g and 0.68 µg/g) respectively for Ikeja and Isolo industrial estate were lower than that obtained in contaminated soils (3865 µg/g) in Albania (Shallar *et al*., 1998) and 2.2 µg/g obtained in top soils in Ibadan, Nigeria (Onianwa *et al*., 2001). The Cd level of (2.0 µg/g) in this study was comparable with levels reported for in Auto-workshops (1.48 µg/g), gas station (1.13 µg/g) and motor packs (1.37µg/g) in Ibadan city (Onianwa *et al*., 2001)

4.10.5 Zinc

Zn concentrations obtained in Tables 4.29 were higher than average control soils levels for Ikeja industrial estate soil while Isolo industrial estate soil (Table 4.32) had its Zn level lower than the control soil but there is no significant difference. The levels of Zn in the study areas were affected by seasonal factors with the dry season having elevated concentrations of the metal (Table 4.35b and 4.36b). The monthly variations of Zn in Figure 4.36 shows month of January 2007 having elevated concentrations of the metal for the study areas. Accumulation factors of 2.4 and 0.9 for Ikeja and Isolo industrial estate soil respectively indicated high level of Zn contamination at the Ikeja industrial estate soil.

Zn levels of 280 µg/g and 50 µg/g around Ikeja and Isolo industrial estate are higher than

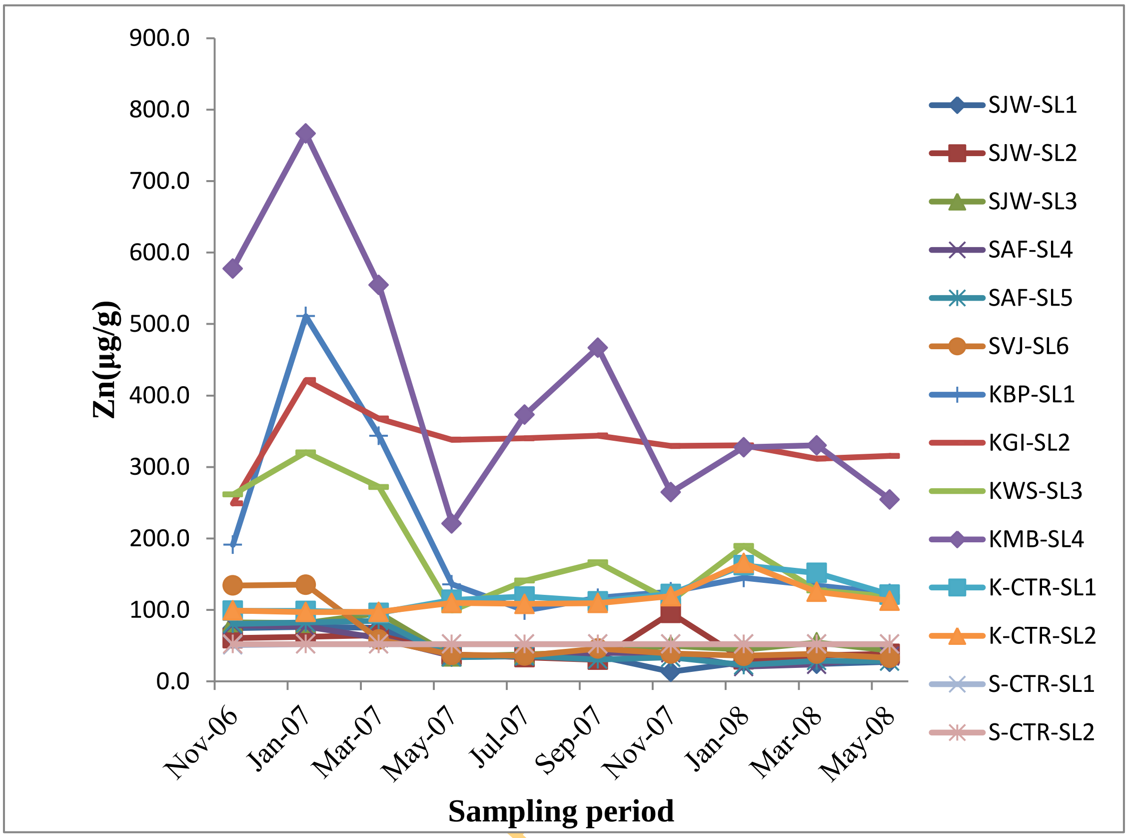

Fig. 4.36: Variations of zinc contents of soils with sampling period.

48µg/g obtained in topsoil in Ibadan Nigeria (Onianwa *et al*., 2001). The average Zn levels in Ikeja industrial estate was higher than that level reported for topsoil in Abakaliki, Nigeria (78µg/g) (Chukwuma, 1996), Hong Kong (59µg/g) (Chen *et al*., 1997).

4.10.6 Copper

The Cu levels in Ikeja and Isolo industrial estate showed seasonal variation as shown in (Table 4.35b and 4.36b) with higher level of Cu in wet season (Figure 4.37). The levels of Cu in soil around Isolo industrial estate are higher than the control (Table 4.32) while the soil around Ikeja industrial estate had lower levels of Cu than the control soil (Table 4.29). Accumulation factors of 0.6 for Ikeja industrial estate and 1.1 for Isolo industrial estate, this indicates low level of Cu contamination in the study area. Average soil Cu level in Ikeja (41µg/g) and Isolo (24µg/g) industrial estate are higher than 17µg/g obtained in top soil of Ibadan Nigeria (Onianwa, 2001), but lower than the average Cu level in Auto workshops (410µg/g), gas stations (117µg/g) and motor parks (59µg/g) in Ibadan city (Onianwa *et al*., 2001).

4.10.7 Chromium

There were no seasonal variation in Cr levels in soil at the Ikeja and Isolo industrial estate (Tables 4.35b and 4.36b). The monthly variation as shown in Figure 4.38, indicated that level of Cr in the control soil sample for Ikeja industrial estate are visibly higher in the metal than the soil around the estate. The level of Cr in the Isolo industrial estate soil shows significantly difference with that of the control soil. Accumulation factor of 0.2 and 0.7 for Ikeja and Isolo industrial soil respectively did not indicate any significant contamination of soil with Cr. Chromium levels were more abundant in soil around Ikeja industrial area and its control compared to Isolo industrial area and its control.

The average Cr level of 18µg/g and 6.5µg/g for Ikeja and Isolo industrial respectively in this study was lower than levels reported in Auto workshops (33.0µg/g), gas station (32.2µg/g) and motor parks (36.3µg/g) in Ibadan city (Onianwa *et al*., 2001)

4.7.8 Nickel

There were no seasonal variations in levels of Ni in the Ikeja and Isolo industrial estate soil. The monthly variations in Ni (Figure 4.39) were similar to that of Cd in which the dry months recorded high level of accumulation of the metal on the top soil.

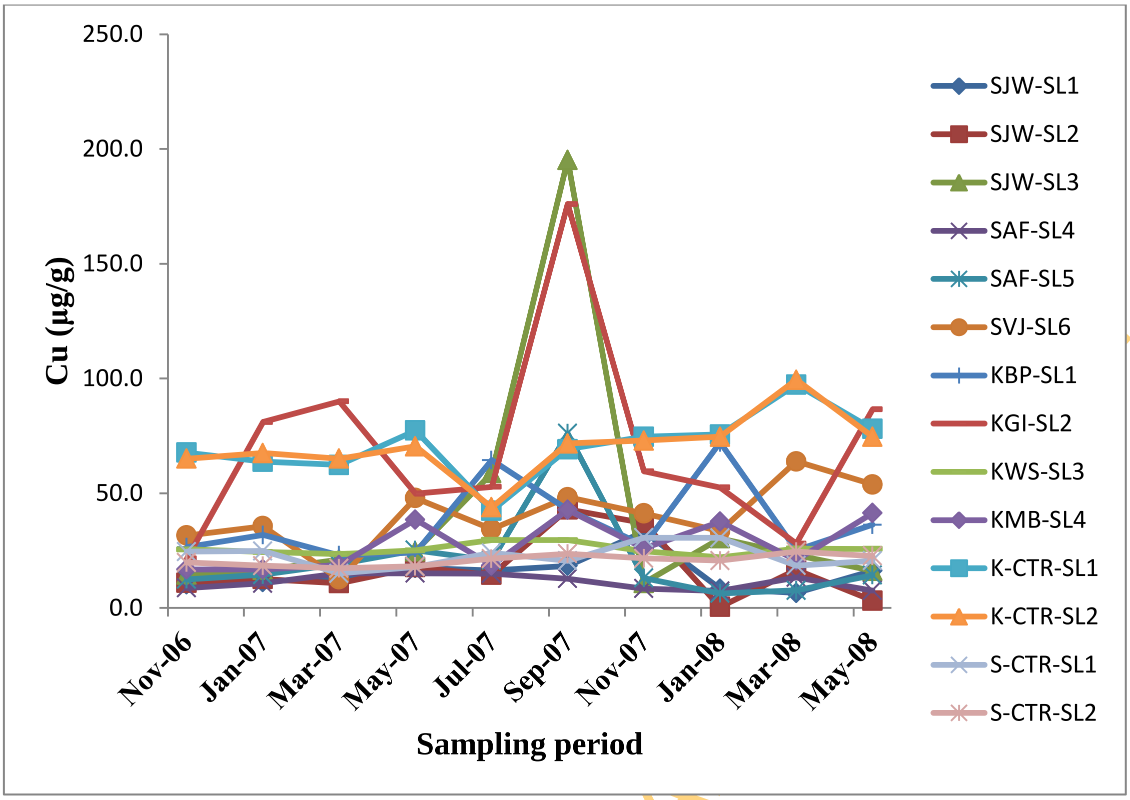

Fig. 4.37: Variations of copper contents of soils with sampling period.

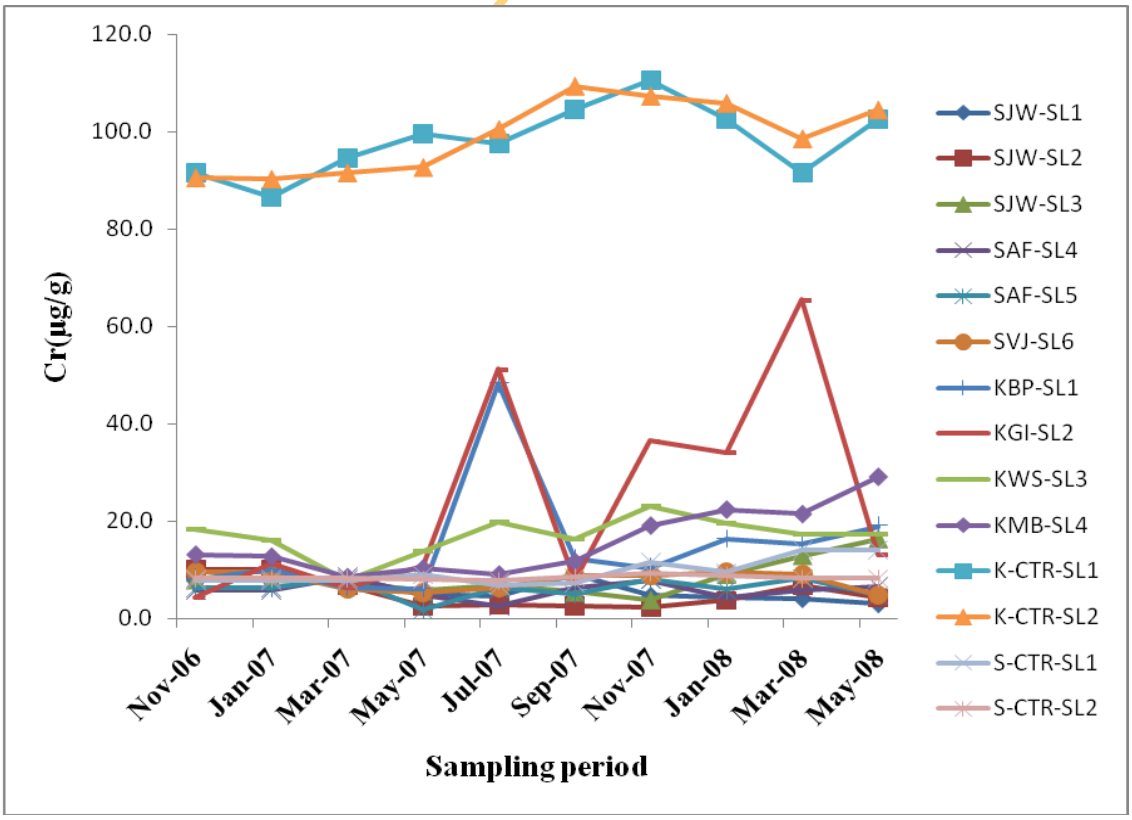

Fig. 4.38: Variations of chromium contents of soils with sampling period.

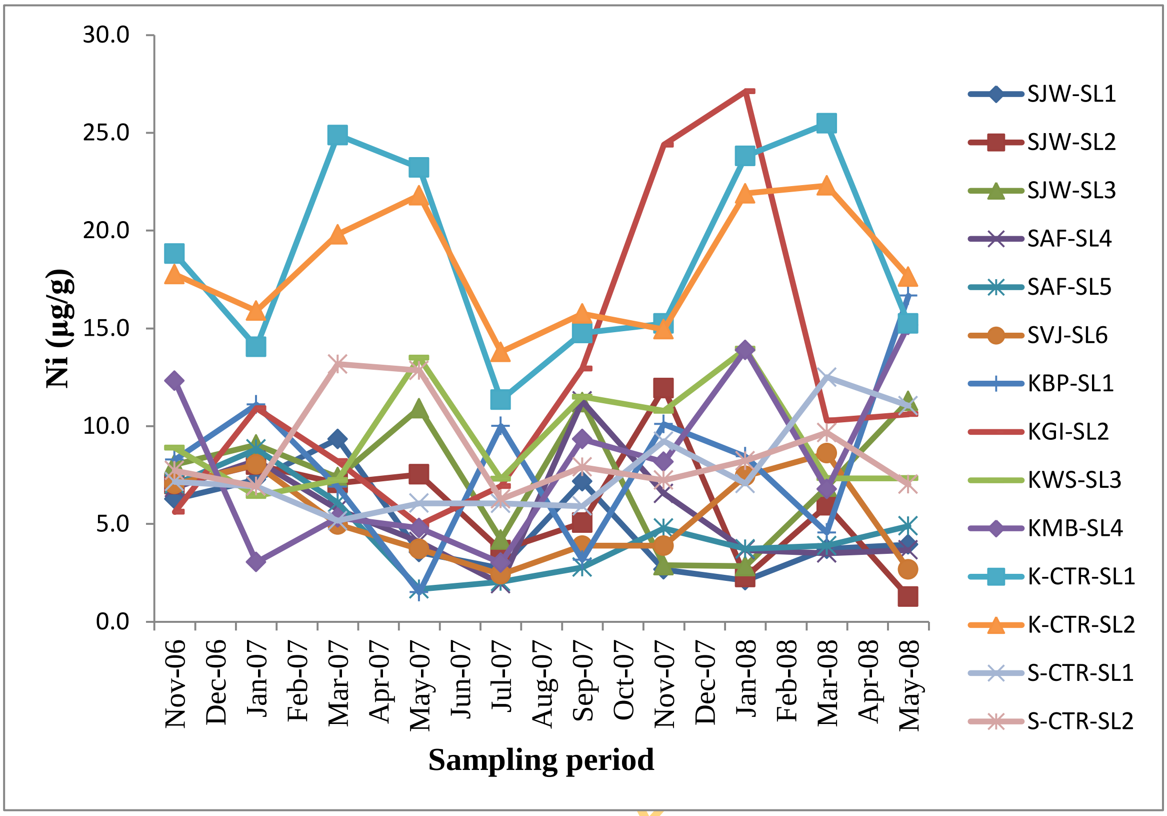

Fig. 4.39: Variations of nickel contents of soils with sampling period.

Nickel levels at the industrial estates had no significant difference with the level in the control soils. The accumulation factor of Ikeja industrial estate soil – 0.6 and that of Isolo industrial estate soil 0.7 further justify the low level of Nickel in the soil around the industrial estate soils. Top soils throughout the world contain background Ni concentration within the broad range of 1 to 100ppm (Kabata and Pendicis, 1984).

The study areas were considered not contaminated since their Ni levels generally fall below 100ppm. The Ni levels of Ikeja industrial estate – 10µg/g and Isolo industrial estate – 5.6µg/g were lower than levels reported for in Auto workshops (15.1µg/g), gas stations (11.1µg/g) and motor parks (11.5µg/g) in Ibadan city (Onianwa *et al*., 2001).Average Ni levels of Ikeja industrial estate compared closely with topsoil of Ibadan. Nigeria (Onianwa, 2001) while Isolo industrial estate soil is lower than soils reported by (Onianwa 2001; Chukwuma, 1996).

4.11: ASSESSMENT OF LEVEL OF CONTAMINATION OF SOILS AROUND THE INDUSTRIAL ESTATE

For a better estimation of anthropogenic input, sampling sites were assessed for the degrees of contamination. Contamination Factors (CF), Pollution load Index (PLI) and Geo accumulation index (Igeo) were used for the estimations.

4.11.1: Assessment of Contamination Factor

Table 4.37 shows the soil contamination factors for the industrial estates studied, (see section 3.14.1)

Where the contamination factor: $CF<1$ refers to low contamination;
$1\leq CF<3$ means moderate contamination;
$3\leq CF\leq 6$ indicates considerable contamination
$CF>6$ indicates very high contamination.

From the contamination factors categories described above, average K-SL had no contamination in all the metals except Cd that is moderately contaminated. Average S-SL suffered very high contamination in Pb level; moderately contamination in Cd and no contamination for Zn, Cu, Cr and Ni.

Table 4.37: Soil contamination factors for the industrial estates studied.

Site Code	**Pb**	**Cd**	**Zn**	**Cu**	**Cr**	**Ni**
K-SL	0.88	1.00	2.39	0.58	0.19	0.56
S-SL	7.00	0.84	0.86	1.10	0.73	0.68

4.11.2: Assessment of Pollution Load Index

Each industrial estate was also evaluated for the magnitude of metal pollution, using the pollution load index (PLI) developed by Thomilson *et al*., (1980) (see section 3.14.2).

The PLI provides simple but comparative means for assessing a site quality, where a value of PLI <1 denote perfection: PL1=1 present that only baseline level of pollutants are present and

PLI>1 would indicate deterioration of site quality.

Average K-SL and Average S-SL pollution load index is 0.712 and 1.18 respectively. The soil metal levels in Ikeja industrial area in terms of pollution load shows perfection while Isolo industrial area indicates deterioration of site with the metals studied.

4.11.3: Assessment of Geo-accumulation Index.

Enrichment of metal concentration above baseline concentration was calculated using the method proposed by (Muller, 1969). Assesses the metal pollution in terms of seven (0 to 6) enrichment classes (Appendix 12) ranging from background concentration to very heavily polluted (see section 3.14.3).

Table 4.38 shows the calculated Geo-accumulation index values. It was evident from the table that the uncontaminated to moderately contaminated I_{geo} value of 0 to 1 of class 1 was observed in K-SL for Zn with value 0.64. S-SL soils show moderately/strongly contaminated of I_{geo} class 3 for Pb in soil (2.20). The other metals analysed had values of I_{geo} <1 which showed non contamination.

Generally, as revealed from the three pollution assessment methods, soil of average S-SL was pollution impacted more than average K-SL.

4.12: TREATMENT OF EFFLUENT

4.12.1 Treatment with Inorganic Coagulants

Treatment with $FeCl_2.4H_2O$: Fig 4.40 shows the trend in COD reduction during treatment with ferrous chloride. An immediate and effective reduction (85%) in COD was obtained on the first day. Thereafter the degree of reduction declined slightly but this varied generally within 60% - 90% during the remaining study period. The reduction in COD was remarkably

Table 4.38: Geoaccumulation index values for metals in soil from the industrial estates studied.

Site Code	Pb	Cd	Zn	Cu	Cr	Ni
K-SL	-0.77	-0.58	0.64	-1.36	-2.90	-1.40
S-SL	2.20	-0.84	-0.84	-0.45	-1.03	-1.14

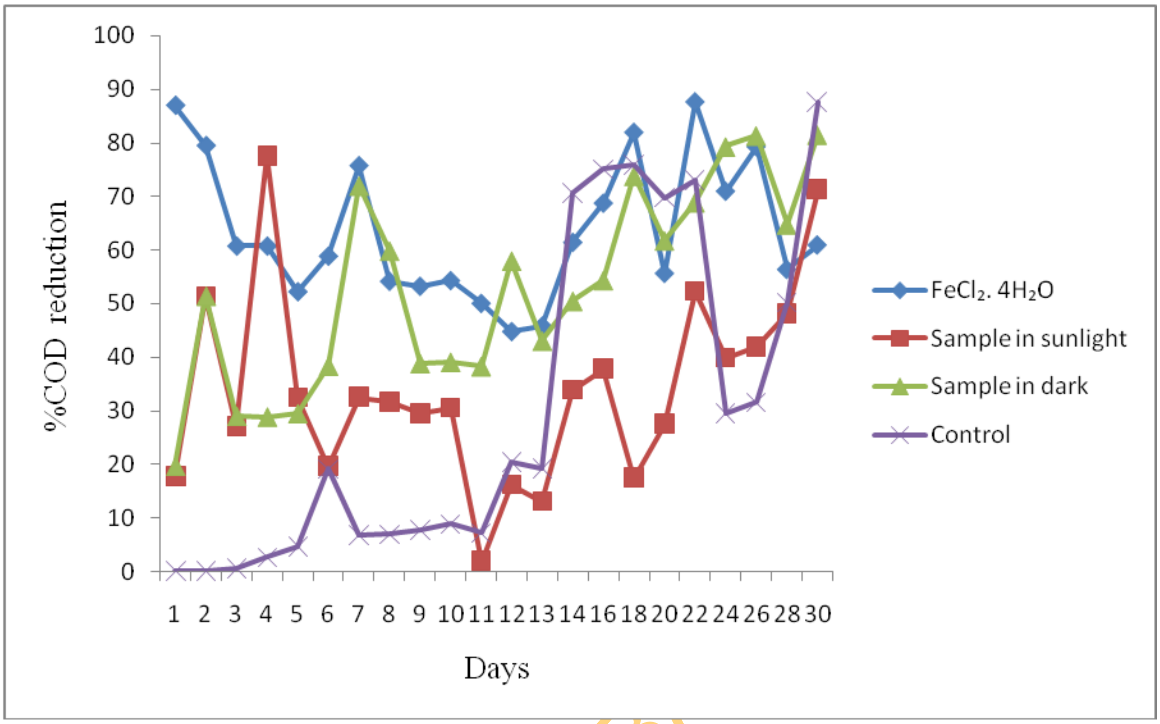

Fig 4.40: Trend in COD reduction during treatment with $FeCl_2.4H_2O$.

different from the control. The coagulant (Fe^{2+}) neutralizes the suspended solids portion from the waste water (usually color-producing organic substances) which carries negative charges, making them less stable in suspension. The flocs formed settle under gravity to the bottom of the jar, hence clearer solution was obtained. The pH of this medium was acidic; this could also have contributed to the coagulation process.

$2FeCl_2 + 2Ca(HCO_3)_2$------------> $2Fe(OH)_2 + 2CaCl_2 + 4CO_2$

Treatment with $FeSO_4.7H_2O$: Fig 4.41 shows the trend in COD reduction during treatment with ferrous sulphate heptahydrate. Day 1 gave 62% reduction in COD while an increase in COD reduction (90%) was observed on Day 2. Subsequently, a decrease in COD reduction was observed till day 16, after which this increased gradually to 90% on Day 22. Optimal reduction level was observed on Day 22.

Basic reactions occurring during the coagulation process for ferrous sulphate is given in the following equation:

$$FeSO_4 + 2HCO_3^- \rightarrow Fe(OH)_2 + SO_4^{2-} + 2CO_2$$

Hydrolysis of $FeSO_4$ during coagulation results in the formation of corresponding gel-like hydroxides and some positively charged mononuclear and poly-nuclear species. These positively charged compounds combine with negatively charged colloidal particles present in the wastewater by charge neutralization mechanism; and at the time of settling under gravity these hydroxides and complexed hydroxides sweep away remaining uncharged/charged colloidal particles of the wastewater with them and precipitate out.

Treatment with combination of $FeCl_2.4H_2O$ and $FeSO_4.7H_2O$: Fig 4.42 shows the trend in COD reduction during treatment with a combination of ferrous chloride pentahydrate and ferrous sulphate heptahydrate. 55% COD reduction was achieved on the first day of application of the coagulants. Subsequently, the effectiveness of treatment decreases and then rose to a maximum of about 89% on Day 22. Thus, an optimal COD reduction was achieved on Day 22. The combination of these coagulants did not give a better COD reduction as compared to when they were singly used.

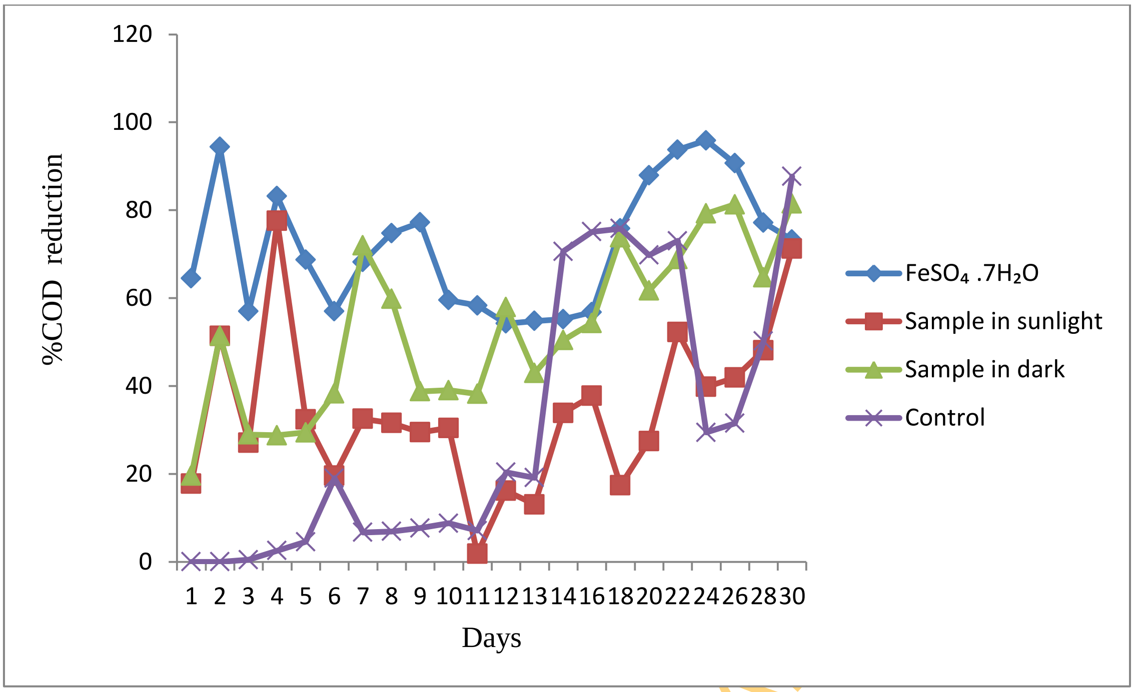

Fig 4.41: Trend in COD reduction during treatment with $FeSO_4.7H_2O$.

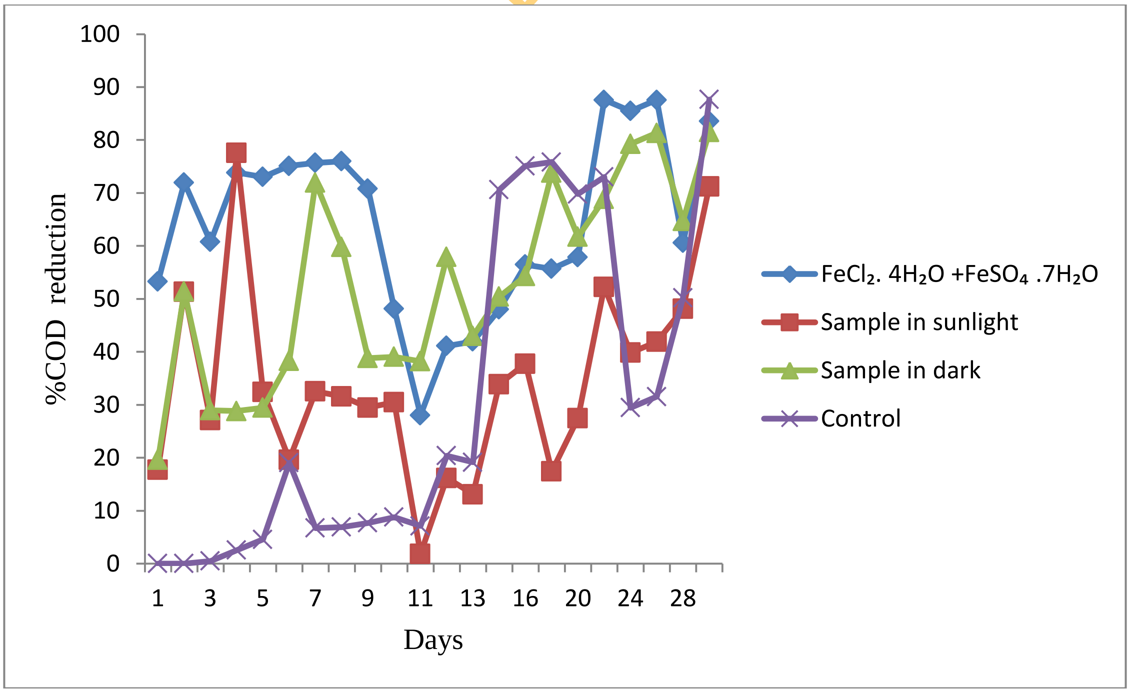

Fig 4.42: Trend in COD reduction during treatment with $FeCl_2.4H_2O$ +$FeSO_4.7H_2O$.

Treatment with $FeCl_3$: The trend in COD reduction during treatment with ferric chloride is illustrated in Fig 4.43. 20% reduction occurred on the first day. The best reduction achievable was an 87% reduction which was achieved on the seventh day. Ferric chloride when added in water yields ferric and chloride ions. Ferric ions neutralise negatively charged colloidal particles and agglomerisation of the colloidal particles can occur or they may combine with hydroxide ions to form ferric hydroxide which adsorbs colloidal particles, providing clarification of effluent.

Treatment with Alum: 62% COD reduction occurred on the first day, and this improved to yield the optimum reduction of 90% on the second day (Fig 4.44).

The trivalent metallic ions (Al^{3+}) combine with hydroxide ion to rapidly form hydroxide precipitate. The colloidal particles formed provide condensation site where the precipitate can form and therefore, the colloid becomes entrapped in the precipitate and settles with it. The pH of the medium is low; therefore an increase in hydrogen ion concentration would neutralize the negative charged carbon surface. This enhances the adsorption of the negatively charged organic species because of reduction in the forces of repulsion between adsorbent and adsorbate.

$A1_2(SO_4)_3 + 3Ca(HCO_3)_2$ ------------> $2Al(OH)_3 + 3CaSO_4 + 6CO_2$

Comparative COD reduction is represented in Figure 4.45 for the inorganic coagulants. It was observed that $FeCl_2.4H_2O$ gave a 86.9% reduction in COD on the first day of the treatment followed by $FeSO_4.7H_2O$ (65.5%), 61.4% Alum, $FeCl_2.4H_2O + FeSO_4.7H_2O$ (53.3%) while $FeCl_3$ gave the least reduction of 15.5%. During the first 14 days of the treatment process, $FeSO_4.7H_2O$ gave a reduction of 66.2% followed by 60.9% for $FeCl_2.4H_2O$; then $FeCl_2.4H_2O + FeSO_4.7H_2O$ achieved59.8%, while $FeCl_3$ gave the least reduction of 20.9%. Subsequently after the first 14 days of monitoring, the average reduction result is in the order of $FeSO_4.7H_2O$> Alum > $FeCl_2$. $4H_2O$ > ($FeCl_2$. $4H_2O + FeSO_4.7H_2O_4$) > $FeCl_3$.

The efficiency of COD reduction was better with the iron salts (ferrous ions) than alum, possibly because the former is a better reducing agent. The results obtained in this study is similar to that obtained by Birdie and Birdie, 1994; Arceivala, 1998; Choudhary and Ojha, 2011. It was reported that a faster sedimentation of sludge by iron salts with lime than alum salt was observed. The sludge formation is as a result of removal of suspended solid which.

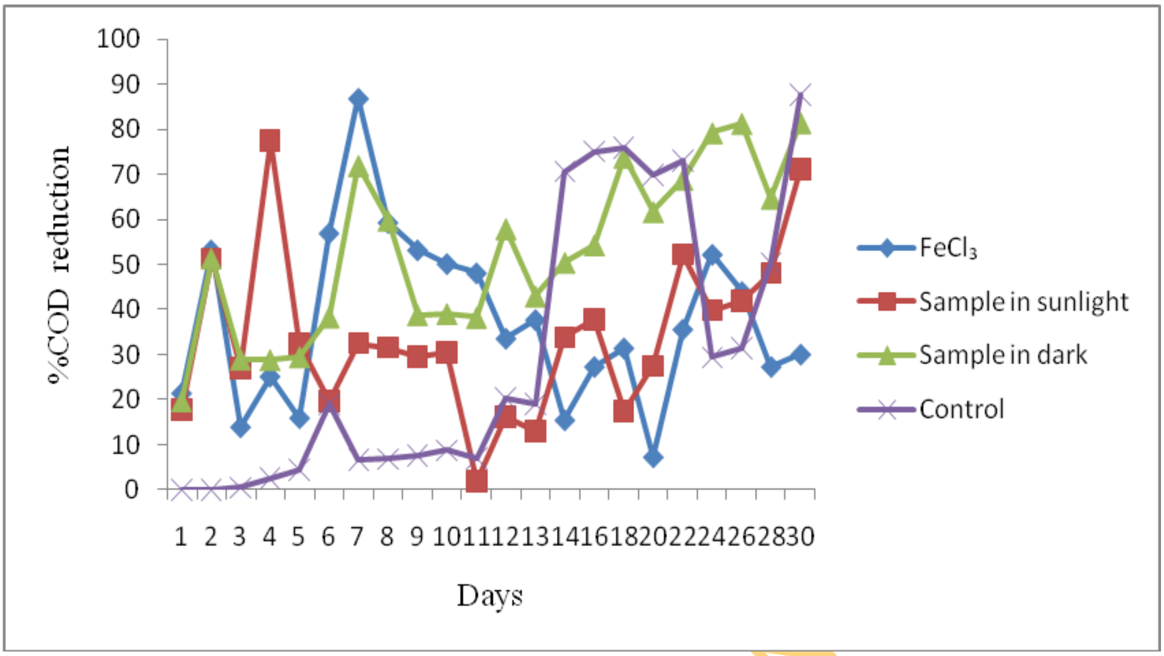

Fig 4.43: Trend in COD reduction during treatment with $FeCl_3$.

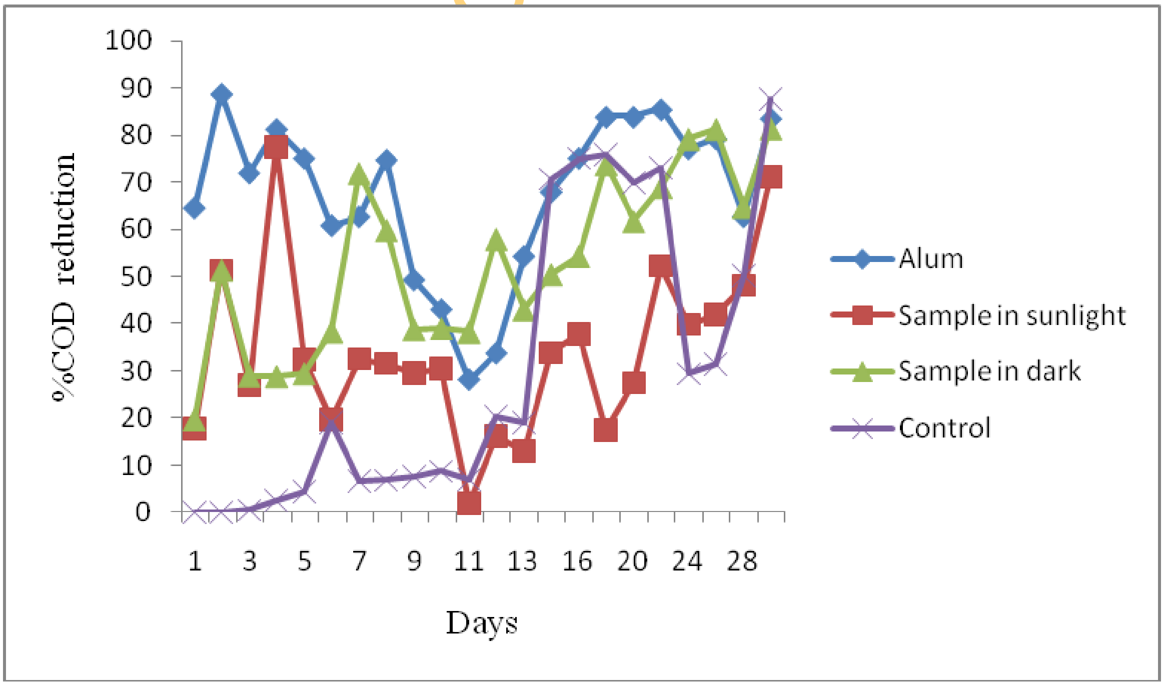

Fig 4.44: Trend in COD reduction during treatment with Alum.

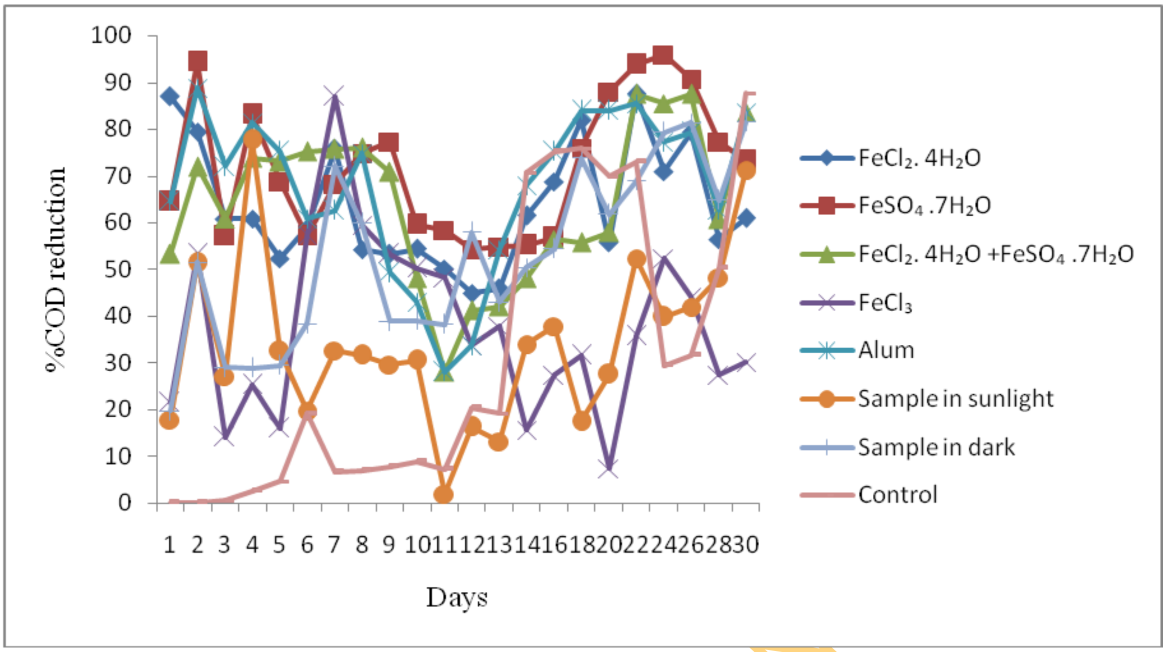

Fig 4.45: Trend in COD reduction during treatment with various inorganic coagulants.

will indirectly affect the reduction of COD.

Generally, the efficiencies of the inorganic coagulants were in the order: $FeCl_2.4H_2O$> $FeSO_4.7H_2O$ > Alum > ($FeCl_2$. $4H_2O$ + $FeSO_4.7H_2O$) > $FeCl_3$.

4.12.2 Treatment with Fenton's Reagent

Treatment with $FeCl_2.4H_2O$ + H_2O_2: Day 1 gave 78% COD reduction followed by an increase in reduction on Day 3 to 90% (Fig 4.46). The effectivenss of COD reduction stabilized at about this value up to the 22nd day.

Treatment with $FeSO_4.7H_2O$ and H_2O_2: Fig 4.47 shows the trend in COD reduction during treatment with $FeSO_4.7H_2O$ and H_2O_2. A 92% reduction was attained even on the first day. There were subsequently minor variations, but the reduction generally stabilised at about this value.even up to the last day

Treatment with $FeCl_2.4H_2O$ + $FeSO_4.7H_2O$ and H_2O_2: Fig 4.48 shows the trend in COD reduction during treatment with $FeCl_2.4H_2O$ + $FeSO_4.7H_2O$ and H_2O_2**.** Day 1 gave 80% COD reduction while an increase in reduction was observed on Day 2 (87%). The degree of reduction varied mildly as time progressed, but eventually stabilized at about 95%

Figure 4.49 compares the COD reduction with the use the various Fenton's reagents. It was observed that $FeSO_4.7H_2O$ + H_2O_2 gave 92.5% reduction on the first day of the treatment, followed by $FeCl_2.4H_2O$ + $FeSO_4.7H_2O$ + H_2O_2 (81.3%) and $FeCl_2.4H_2O$ + H_2O_2 (75.7%). During the first 14 days of the treatment, the trend in the reductions was in the order: $FeSO_4.7H_2O$ + H_2O_2 (64.7%) > $FeCl_2.4H_2O$ + $FeSO_4.7H_2O$ + H_2O (56.5%) > FeCl2.4H2O + H_2O_2 (41.8%).

The principle/reactions behind the application of Fenton's reagent for this purpose derive from the following (Wardman and Candeias, 1996):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \text{ (chain initiation)} \qquad (1)$$

The ferrous iron (Fe^{2+}) starts the reaction and catalyses the decomposition of H_2O_2

$OH^{\bullet} + Fe^{2+} \rightarrow OH^{-} + Fe^{3+}$ (chain termination) (2)

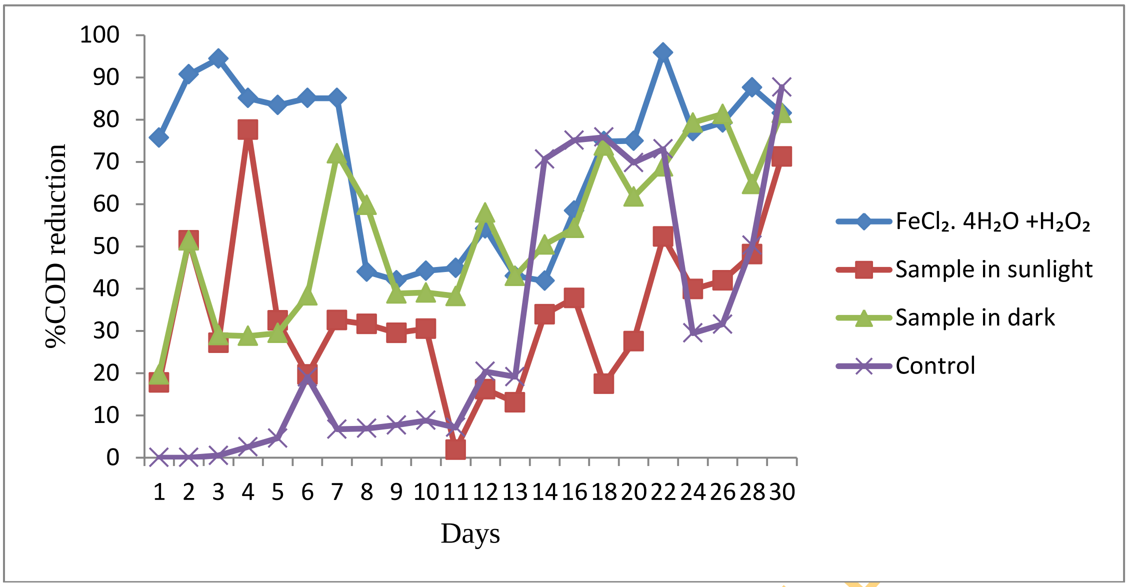

Fig 4.46: Trend in COD reduction during treatment with $FeCl_2.4H_2O + H_2O_2$.

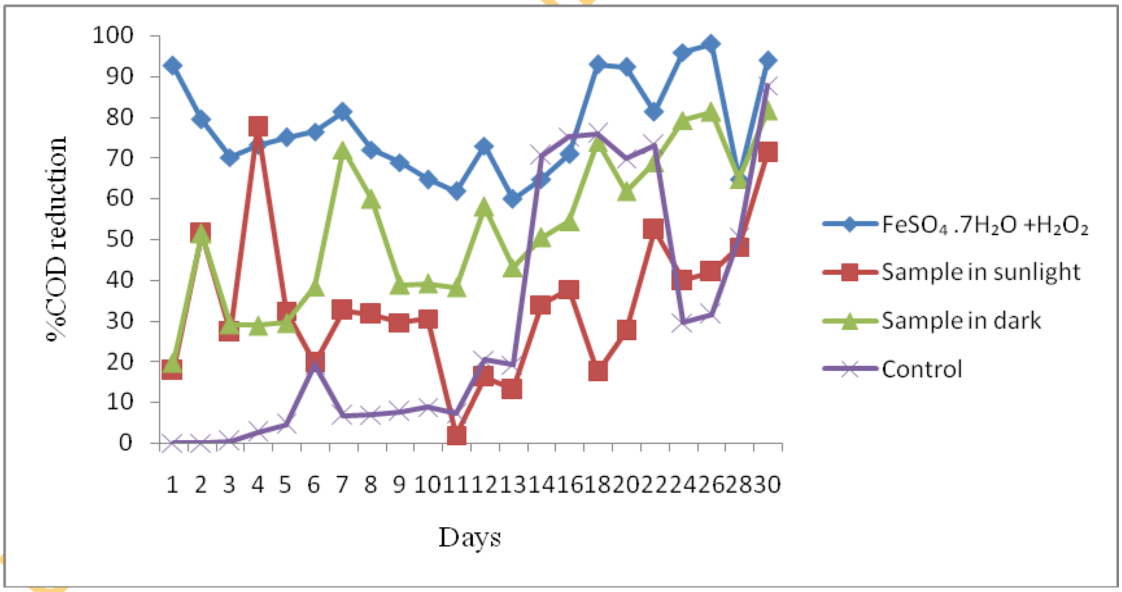

Fig 4.47: Trend in COD reduction during treatment with $FeSO_4.7H_2O + H_2O_2$.

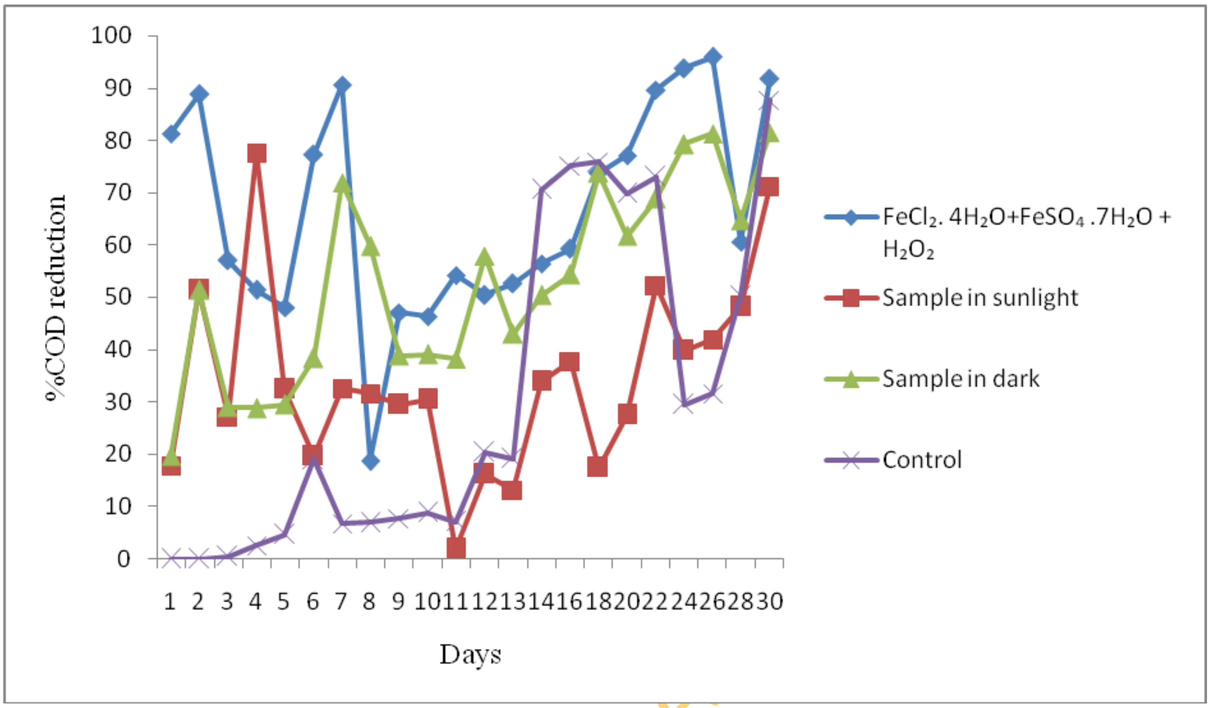

Fig 4.48: Trend in COD reduction during treatment with $FeCl_2.4H_2O$ +$FeSO_4.7H_2O$ + H_2O_2.

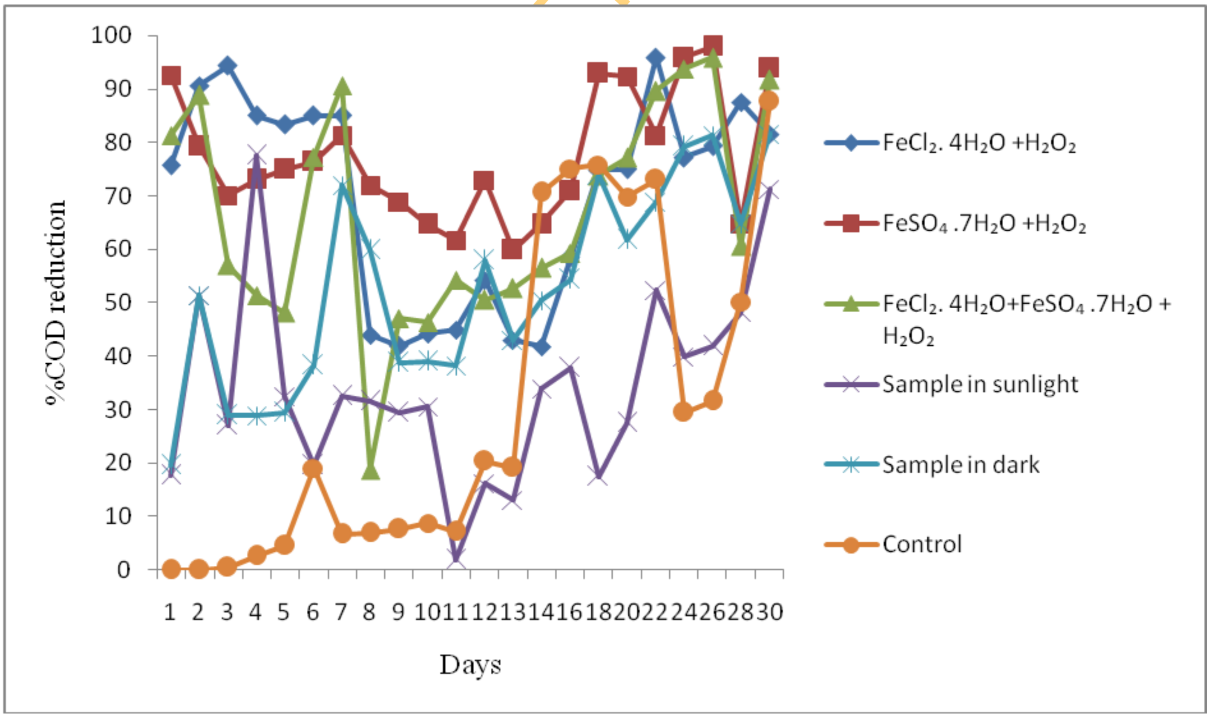

Fig 4.49: Trend in COD reduction during treatment with Fenton's reagents.

Hydroxyl radicals react with ferrous ion to form hydroxide and ferric ions.

The formed ferric ions (Fe^{3+}) decompose hydrogen peroxide in water and oxygen (forming ferrous ions and radicals):

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe - OOH^{2+} + H^+ \quad (3)$$

$$Fe - OOH^{2+} \leftarrow HO_2^{\bullet} + Fe^{2+} \quad (4)$$

The radical formed reacts with organics (RH) by abstraction of proton from the organic to form organic radicals ($R^{\bullet}$).

$$RH + OH^{\bullet} \rightarrow H_2O + R^{\bullet} + \text{further oxidation}$$

4.12.3 Treatment with Charcoal

Reduction during treatment with charcoal was 18% on Day 1. A gradual increase occurred, and up to 90% reduction was achieved by Day 22 (Fig 4.50). Charcoal treatment option performed better than simple exposure to darkness or sunlight.

Generally, the sample kept in the dark gave a better COD reduction on Day 1 (19.6%) compared to the sample kept in sunlight, this could be as result of activities of microorganism.

Summarily, the order of efficiencies of the various chemicals used was: Fenton's reagent > $FeCl_2.4H_2O$ > $FeSO_4.7H_2O$ > $FeCl_2.4H_2O$ + $FeSO_4.7H_2O$ > alum > activated charcoal > $FeCl_3$.

4.12.4: pH Variation during Treatment of Textile Effluent

Figure 4.51 shows the variation of pH values during treatment of the effluent with various coagulants. The initial pH of the textile effluent before treatment was 10.4. On Day 1 of the treatment, the samples that were treated with inorganic and Fenton's reagent were acidic while the samples kept in the dark, sunlight and treated with activated charcoal gave basic values. As treatment progressed, the treatments with sunlight, exposure to the dark, and addition of charcoal gave pH range within the FEPA regulatory guideline for wastewater (6-9), while the other treatment options yielded acidic effluents. Therefore, the use of activated charcoal for the regulation of pH for textile effluent may be encouraged.

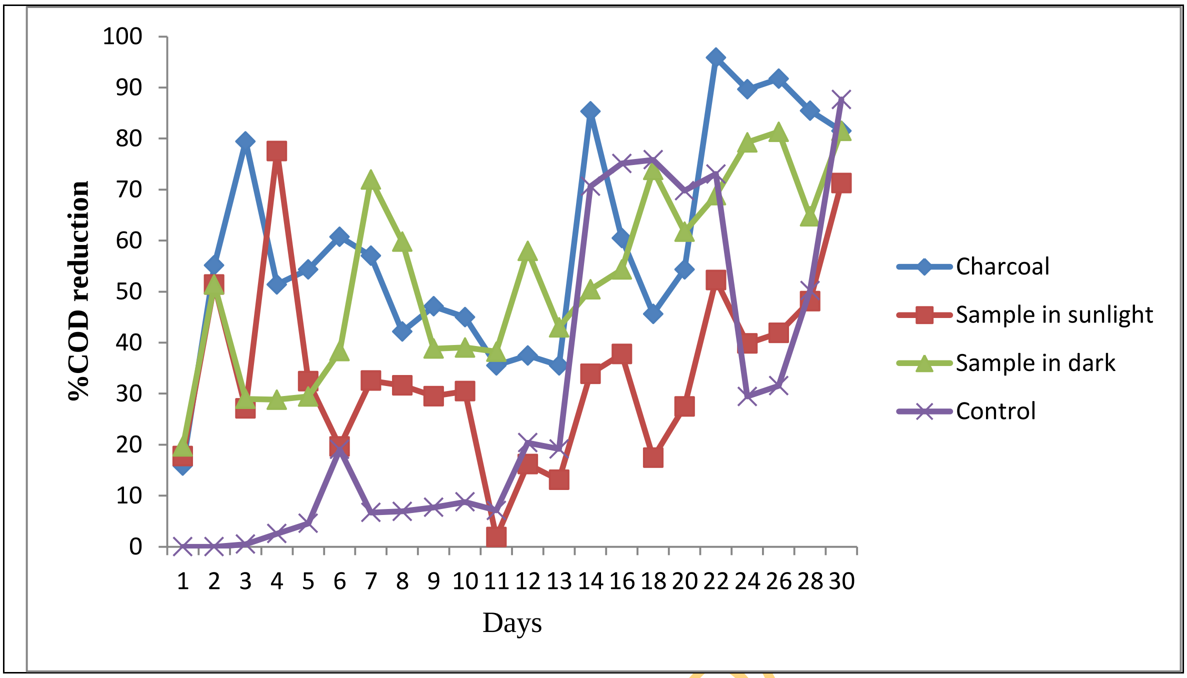

Fig 4.50: Trend in COD reduction during treatment with charcoal.

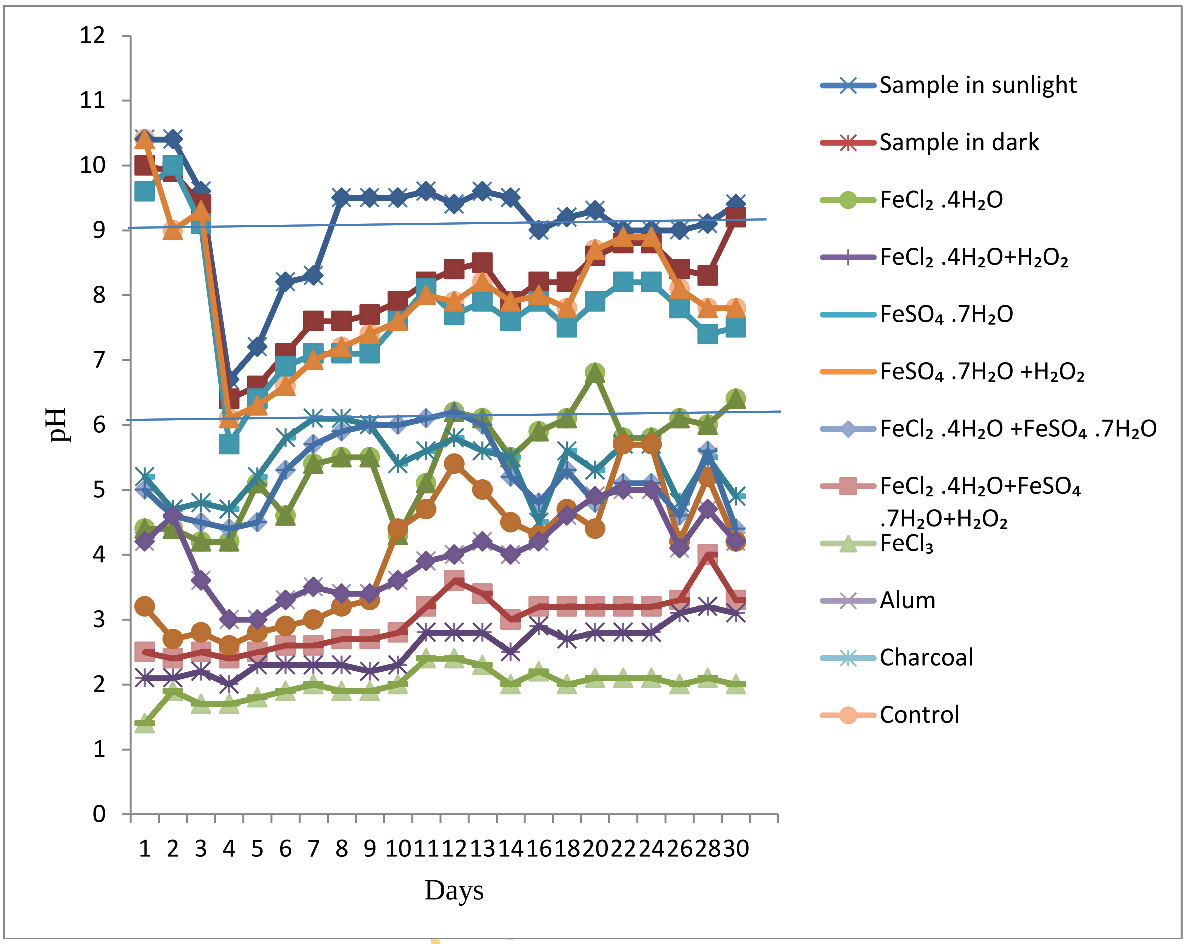

Fig 4.51: Variations in pH values during various treatment options.

4.12.5: TDS Variation during Treatment of Textile Effluent

Table 4.39 shows the variation of TDS levels during treatment of textile effluent. The initial TDS of the effluent before treatment was 780 mg/L. On the first day of treatment, treatment options of $FeCl_2.4H_2O + H_2O_2$, $FeCl_2.4H_2O + FeSO_4.7H_2O + H_2O_2$ and $FeCl_3$ gave increase in value of TDS as 1254, 874 and 1425 mg/L respectively while the other treatment gave a lower value compared with the control.

Similarly, the treatment options of light, dark, $FeCl_2$. $4H_2O$, $FeSO_4.7H_2O$, $FeSO_4.7H_2O + H_2O_2$, $FeCl_2$. $4H_2O + FeSO_4.7H_2O$, alum and activated charcoal gave reduction in TDS values as the treatment days progressed while the other treatment options had increase in value as the treatment days progressed. The order of reduction in TDS was: $FeCl_3$ > ($FeCl_2.4H_2O + FeSO_4.7H_2O + H_2O_2$) >($FeCl_2.4H_2O + H_2O_2$) > ($FeSO_4.7H_2O + H_2O_2$) > ($FeCl_2$. $4H_2O + FeSO_4.7H_2O$) > $FeCl_2$. $4H_2O$ > alum > activated charcoal > $FeSO_4.7H_2O$.

The effectiveness is in order of $FeSO_4.7H_2O$ > alum = ($FeCl_2$. $4H_2O + FeSO_4.7H_2O$) > charcoal = $FeCl_2$. $4H_2O$ = ($FeSO_4.7H_2O + H_2O_2$) > ($FeCl_2.4H_2O + FeSO_4.7H_2O + H_2O_2$) > ($FeCl_2.4H_2O + H_2O_2$) > $FeCl_3$.

4.12.6: TSS Variation during Treatment of Textile Effluent

Table 4.40 shows the variation of TSS during the treatment of textile effluent. The initial TSS level of the raw effluent before treatment was 135 mg/L. The various treatment options all had increase in the value of TSS throughout the treatment days. This could be associated to suspension of some of the coagulated particles. The TSS could be taken care of by passing the treated effluent through sand filter before discharging into an open sewer.

4.13 ESTIMATES OF GROSS ORGANIC POLLUTION AND EUTROPHICATION POTENTIAL.

4.13.1 Model Result of Multiple Linear Regressions of Physicochemical Data for Predictive Estimation of Concentration of a Gross Organic Pollutant (as COD).

The Multiple Linear Regression Analysis between “gross organic pollution” in the form of COD, and the other explicative variables extracted from the Factor Analysis presented the final regression equations as expressed in Table 4.41.

TABLE 4.39: Changes in TDS (mg/L) values during treatment of textile effluent

Treatment Options/Date	**Day 1**	**Day 2**	**Day 3**	**Day 4**	**Day 5**	**Day 6**	**Day 7**	**Day 8**	**Day 9**	**Day 10**	**Day 11**
Sample in Light	760	684	798	760	570	608	741	646	836	874	722
Sample in Dark	779	684	684	646	494	532	608	627	627	627	646
$FeCl_2$.$4H_2O$	760	893	1045	950	779	741	665	684	627	684	646
$FeCl_2.4H_2O$ +H_2O_2	1254	1311	1425	1368	1045	1121	1083	1140	1007	1045	874
$FeSO_4$.$7H_2O$	684	589	855	779	475	532	608	494	323	494	437
$FeSO_4.7H_2O$ +H_2O_2	760	722	950	912	646	703	665	703	570	589	475
$FeCl_2.4H_2O$ +$FeSO_4$.$7H_2O$	703	646	855	855	589	589	608	532	570	532	285
$FeCl_2.4H_2O$ +$FeSO_4.7H_2O$ +H_2O_2	874	836	1064	1045	684	817	798	855	684	760	627
$FeCl_3$	1425	1444	1900	1805	1235	1406	1425	1539	1292	1121	912
Alum	703	703	988	988	646	741	722	760	684	722	646
Charcoal	760	684	988	665	418	570	589	608	627	589	532
Control	703	646	665	665	513	589	570	570	570	627	551

TABLE 4.39 contd.:

Treatment options/Date	**Day 12**	**Day 13**	**Day 14**	**Day 16**	**Day 18**	**Day 20**	**Day 22**	**Day 24**	**Day 26**	**Day 28**	**Day 30**
Sample in Light	703	798	950	893	893	912	855	836	855	817	912
Sample in Dark	551	627	665	608	684	665	665	608	627	684	589
$FeCl_2 .4H_2O$	570	627	570	608	646	665	627	627	646	513	703
$FeCl_2.4H_2O + H_2O_2$	874	950	912	874	950	969	931	912	798	722	741
$FeSO_4 .7H_2O$	475	456	551	494	532	513	532	475	475	532	570
$FeSO_4.7H_2O + H_2O_2$	494	532	627	551	627	646	608	912	532	532	608
$FeCl_2.4H_2O + FeSO_4 .7H_2O$	475	551	551	570	627	589	570	551	475	570	627
$FeCl_2.4H_2O + FeSO_4.7H_2O + H_2O_2$	627	703	684	665	741	931	722	608	532	532	722
$FeCl_3$	1273	1368	1368	1368	1425	1539	1501	1444	1045	570	1140
Alum	608	684	665	627	703	722	665	608	551	950	342
Charcoal	684	608	608	589	646	646	627	570	893	266	551
Control	551	608	646	570	646	646	646	570	589	589	551

TABLE 4.40: Changes in TSS (mg/L) value during treatment of textile effluent.

Treatment Options/Date	**Day 0**	**Day 2**	**Day 4**	**Day 6**	**Day 8**	**Day 12**	**Day 16**	**Day 20**	**Day 24**	**Day 28**
Sample in Light	135	1040	1035	1009	880	850	705	680	500	500
Sample in Dark	135	400	550	864	790	785	610	640	500	500
$FeCl_2 .4H_2O$	135	440	570	429	402	425	650	720	300	302
$FeCl_2 .4H_2O + H_2O_2$	135	1200	1020	1344	1100	1050	805	320	250	255
$FeSO_4 .7H_2O$	135	400	580	984	890	780	605	320	400	402
$FeSO_4 .7H_2O + H_2O_2$	135	400	575	740	690	580	530	380	700	705
$FeCl_2 .4H_2O$ + $FeSO_4 .7H_2O$	135	280	300	380	350	345	310	280	300	306
$FeCl_2 .4H_2O$ + $FeSO_4 .7H_2O + H_2O_2$	135	280	340	620	615	600	390	360	400	410
$FeCl_3$	135	1280	1080	884	870	850	390	400	200	220
Alum	135	400	420	280	300	290	395	400	1700	1500
Charcoal	135	1320	1420	1590	1285	1109	210	200	250	240
Control	135	1360	1420	1672	1492	1290	390	320	500	510

Table 4.41: Result of multiple linear regression of physicochemical data for predictive estimation of COD as indicator of gross organic pollution.

Site code	Effluent Types	Equation	R^2
KJE-EFF	Mixed industries	$COD = 0.123\ Cond - 8.713\ TH$	0.954
KHO-EFF	Basic metal	$COD = 531 - 0.054\ Cond - 2.257\ TH - 4.897 Mg + 2.580 Cl^- + 117\ PO_4^{3-}$	0.905
KBP -EF	Paint industry	$COD = 3468 - 4.75\ SO_4^{2-} - 9.12\ Cl^- + 4.82\ TH - 0.033\ Cond$	0.740
KGI-EF	Basic metal	$COD = 418 + 0.017\ Cond - 2.585\ NO_3^{--}$	0.770
KWS-EF	Textile industry	$COD = 655 - 0.027\ Cond - 21.7\ Mg$	0.698
SJW-EF	Pharmaceutical industry	$COD = 0.390\ TDS - 0.450\ Alk - 10.79\ SO_4^{2-} + 31.07\ NO_3^{--}$	0.933
SAF-EF	Pharmaceutical industry	$COD = 0.007\ Cond$	0.932
SVJ-EF	Food & beverages industry	$COD = 0.415 - 0.008\ TDS + 0.024\ SO_4^{2-} + 0.076\ NO_3^{--}$	0.999
LPZ-EF	Conglomerate	$COD = 0.855\ TDS$	0.638
LCA-EF	Mixed industries	$COD = 6.943\ Ca + 16.14\ Mg$	0.846

These determination coefficients R^2 for gross organic pollutant (COD) ranged within 0.638-0.999. This means that 63.8% - 99.9% dependent variable (COD) variance was explained by the independent variables (parameters reflected in the final equation). With the regression equations generated from the data obtained in the analysis of the various effluents, the gross organic pollutant (COD) can be estimated from the equations.

4.13.2 Model Results of Multiple Linear Regression of Physicochemical Data for Predictive Estimation of Eutrophication Potential (via Phosphate Levels)

The equations obtained for the various effluent types are represented in Table 4.43. The independent variables that are retained in the final equations are different for various effluents. The regression values as shown in Table 4.42 ranged within 0.301-0.999 with KHO-EF (Basic metal Industry) having the least value while KBP-EF (Paint Industry) had the highest R^2 value.

Table 4.42: Result of multiple linear regression of physicochemical data for predictive estimation of phosphate as indicator of eutrophication potential.

Site Code	**Effluent Types**	**Equation**	**R²**
KJE-EFF	Mixed industries	$PO_4^{3-} = 0.03\ Alk - 0.078\ Mg + 0.004TH + 0.002\ Cl^-$	0.970
KHO-EFF	Basic metal	$PO_4^{3-} = 0.642 - 0.004\ Cl^-$	0.301
KBP -EF	Paint industry	$PO_4^{3-} = 1.370 + 0.001\ Alk + 0.015\ Mg - 0.001\ BOD - 0.011\ Cl^- -0.002\ SO_4^{2-} + 0.001\ NO_3^- +0.007\ Ca$	0.999
KGI-EF	Basic metal	$PO_4^{3-} = 2.368 + 0.060\ Ca - 0.395\ Mg$	0.640
KWS-EF	Textile industry	$PO_4^{3-} = 0.704\ ^- + 0.05\ NO_3^-$	0.493
KMB-EF	Pharmaceutical industry	$PO_4^{3-} = 0.00001\ Cond - 1.479\ COD$	0.714
SJW-EF	Pharmaceutical industry	$PO_4^{3-} = 11.848 - 0.025\ TDS + 0.045\ Alk + 1.245\ SO_4^{2}- - 2.232\ NO_3^- + 0.038\ Cl^- + 0.044\ COD - 0.221\ BOD.$	0.981
SAF-EF	Pharmaceutical industry	$PO_4^{3-} = 0.012\ Alk - 1.375\ SO_4^{2}\ - 1.856\ NO_3^-$	0.954
SVJ-EF	Food & beverages industry	$PO_4^{3-} = 0.273 + 0.005Alk -0.109\ COD$	0.917
LPZ-EF	Conglomerate	$PO_4^{3-} = 0.046\ Cl^- + 0.006\ TH + 0.008\ SO_4^{2}- - 0.001\ Alk - 0.032\ Mg - 0.000006COD - 0.173$	0.998
LCA-EF	Mixed industries	$PO_4^{3-} = 0.006\ Alk$	0.939

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 SUMMARY AND CONCLUSIONS

5.1.1 Effluent Characteristics

Most of the effluents had high levels of nitrate COD and BOD, which is indicative of a high level of gross organic pollution, and likelihood to cause eutrophication of receiving water bodies. Chromium and copper were also problematic in textile effluents. In most cases, the characteristics of the effluents did not meet the required limiting guidelines of the regulatory agency in Nigeria. However, the textile and pharmaceutical industrial sector tended to discharge the most polluted effluents. Seasonal variation was not an important factor in determining effluent qualities.

5.1.2 Pollution of Sediments of Effluent Channels

The sediment quality of the effluent channels showed some level of contamination with heavy metals, which correlated with the levels in the effluents. Chromium and zinc were generally more significant in this respect.

5.1.3 Soil Pollution

Soil pollution with heavy metals was not significant, and did not appear to be correlated with levels in effluents and sediments.

5.1.4 Effluent Treatment

Fenton’s reagent was very effective for the treatment of the textile effluents, achieving a COD reduction of about 90% within the first day of treatment. Treatment with ferrous chloride was the second best of the chemical treatment options investigated.

5.1.5 Model Estimation of COD and Phosphate

Various equations have been generated for various effluent types, that can serve as a future means of estimating eutrophication potential (phosphate level) and gross organic pollution load (COD levels) in which data for effluent quality are available.

5.2 RECOMMENDATIONS

(i) Regulatory bodies should enforce the standard regulatory limits for effluents discharge to land and water bodies. Results from this study show that the industries are currently mostly not compliant.

(ii) The model derived from this study for estimating gross organic pollution and eutrophication potential should be further developed to make it more accurate and applicable to estimating other important parameters.

(iii) Studies should be extended to other industrial estates and industry types in the metropolis.

(iv) The chemical treatment options investigated should be applied to real field conditions, with the support of government agencies and the industries involved. This is currently impracticable because the industries resist "intrusion" into their premises for environmental investigations.

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Appendix 1: Coordinates of the sampling locations.

Name of Industrial Estate	Industry Sampled	Coordinates of the Sampling Location	Elevation above Sea level
Ikeja industrial estate	Hoesch Pipe Mills Ltd.	N 06° 36′ 02.8″ E 003° 19′ 50.1″	40 m
Ikeja industrial estate	Berger Paints (Nigeria) Plc	N 06° 06′ 50.9″ E 003° 20′ 09.0″	45 m
Ikeja industrial estate	Galvanizing Industries Limited	N 06° 36′ 46.0″ E 003° 20′ 09.5″	45 m
Ikeja industrial estate	Woolen and Synthetic Textile Manufacturing Limited	N 06° 36′ 37.6″ E 003° 20′ 10.3″	42 m
Ikeja industrial estate	May&Baker (Nigeria) Plc	N 06° 36′ 32.7″ E 003° 20′ 18.5″	47 m
Ikeja industrial estate	Central Treatment Plant	N 06° 36′ 33.0″ E 003° 19′ 54.9″	49 m
Isolo industrial estate	Johnson Wax Nig. Ltd	N 06° 31′ 32.7″ E 003° 19′ 32.7″	23 m
		N 06° 31′ 31.2″ E 003° 19′ 48.9″	20 m
		N 06° 31′ 28.5″ E 003° 19′ 48.6″	18 m
Isolo industrial estate	Afrab Chem	N 06° 31′ 25.4″ E 003° 19′ 48.3″	16 m
		N 06° 31′ 24.4″ E 003° 19′ 48.1″	20 m
Isolo industrial estate	Viju industries	N 06° 31′ 35.5″ E 003° 20′ 04.1″	39 m
Ilupeju industrial estate	PZ Industries Nig. Plc	N 06° 33′ 11.7″ E 003° 21′ 24.7″	32 m
		N 06° 33′ 09.9″ E 003° 21′ 25.6″	29 m
		N 06° 33′ 09.2″ E 003° 21′ 27.8″	31 m
Ilupeju industrial estate	Canal *	N 06° 32′ 57.9″ E 003° 21′ 26.9″	29 m
		N 06° 34′ 56.9″ E 003° 21′ 26.0″	33m

* Canal receives effluents from industries

Appendix 2: Effluent channel of Hoesch Pipe Mill Ltd in Ikeja Industrial Estate

Appendix 3: Effluent channel of May & Baker Nigeria Ltd in Ikeja Industrial Estate

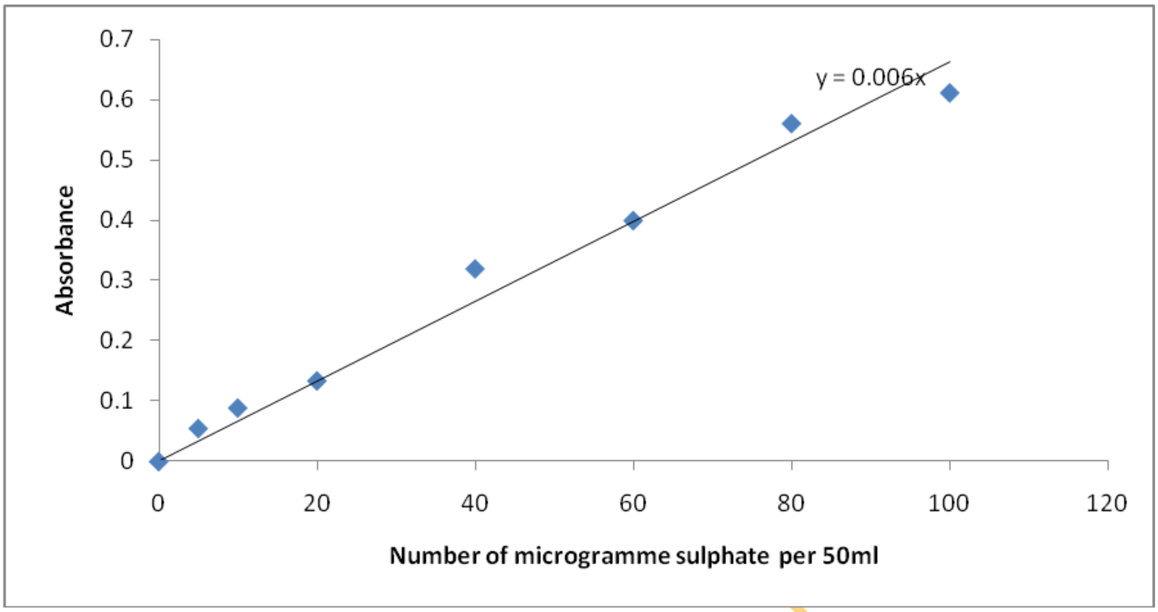
Appendix 4: Effluent channel at the central treatment plant receiving all effluents in Ikeja Industrial Estate.

Appendix 5: Effluent channel of Johnson Wax in Isolo Industrial Estate.

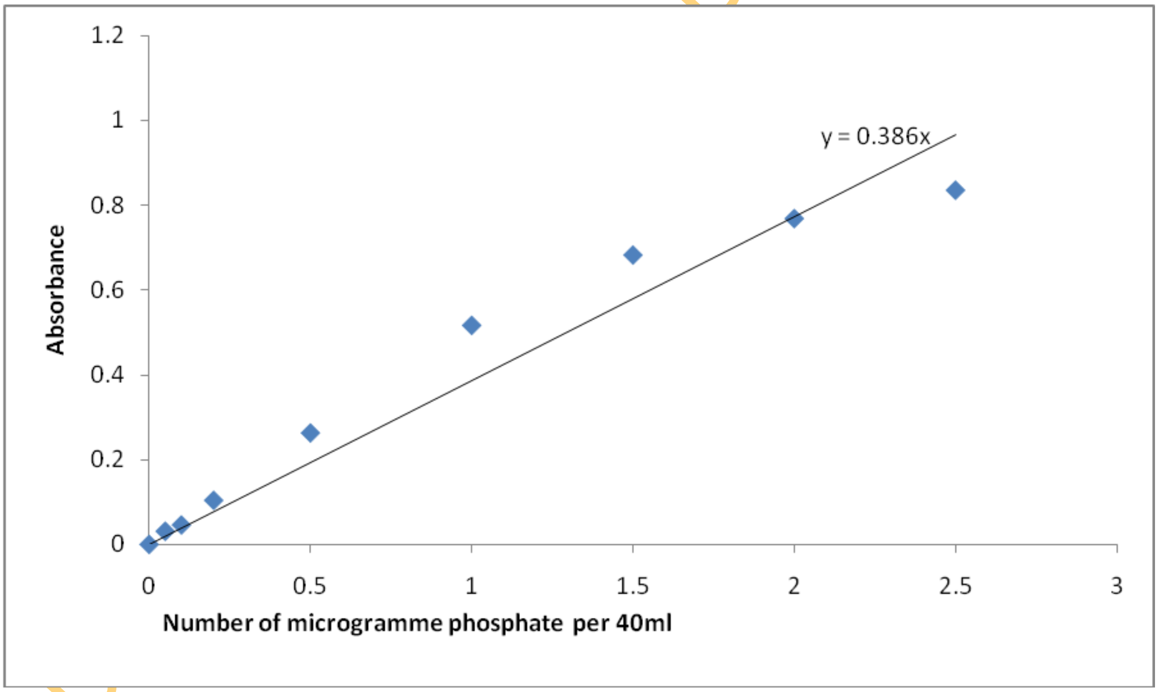
Appendix 6: Effluent channel of Afrab Chem in Isolo Industrial Estate.

Appendix 7: Effluent channel of PZ in llupeju Industrial Estate

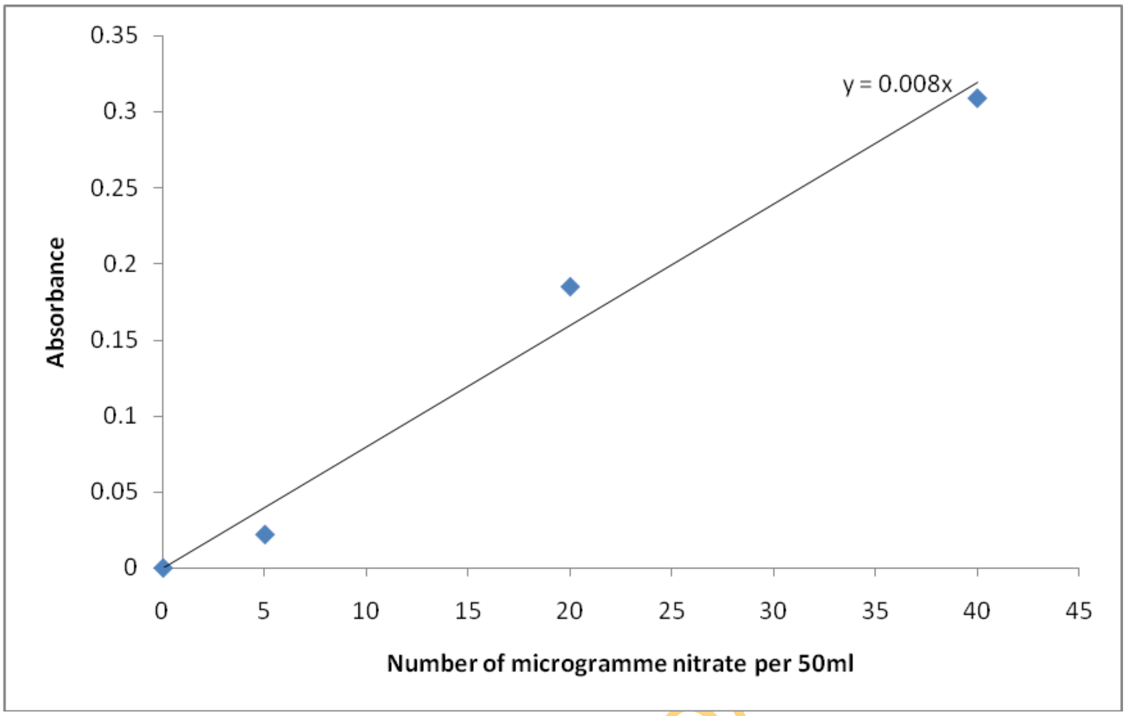
Appendix 8: A canal receiving wastewater from several industries in llupeju Industrial Estate.



Appendix 9: Calibration graph for determination of sulphate.



Appendix 10: Calibration graph for determination of phosphate.



Appendix 11: Calibration graph for nitrate.

Appendix 12: Geo-accumulation index of heavy metals in soil.

I-geo	I-geo. Grade	Soil Quality
5-10	6	Extremely contaminated
4-5	5	Strong/ extremely contaminated
3-4	4	Strongly contaminated
2-3	3	Moderately/ Strongly contaminated
1-2	2	Moderately contaminated
0-1	1	Uncontaminated/ moderately contaminated
<0	0	Uncontaminated