© IJCIRAS | ISSN (O) - 2581-5334
September 2019 | Vol. 2 Issue. 4

# PHYSICO-CHEMICAL ASSESSMENT OF EFFLUENT DISCHARGES FROM CEMENT MANUFACTURING INDUSTRIES ON SURFACE GROUND WATER AND CORRELATIONAL ANALYSIS WITH CONDUCTIVITIES AND TOTAL DISSOLVED SOLIDS;

# CASE STUDIES OF EWEKORO AND SAGAMU, OGUN STATE NIGERIA.

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**Abstract**

***All chemical manufacturing industries generate wastes either in the form of solid, liquid (effluent) or gaseous as they adversely pollute our immediate environments with severe consequences. Portland cement which is specifically and extensively used in various constructions is a potential source of surface water pollution being a mixture of Calcium oxide, Aluminum oxide, silica, Magnesium oxide, and heavy metals. Case studies of two cement factories in Ogun state, southwest Nigeria were analyzed against FEPA standard of 1995. Physico-chemical parameters such as, temperature, pH, BOD, TDS, EC, sulphate, chloride and nitrate of two the cases as [Ewekoro = 30oC, 7.6, 7.67mg/l, 257mg/l,395.38µS/cm, 166.03mg/l,15.5mg/l, 16.3mg/l;Sagamu=33oC,9,8.99mg/l, 255.09mg/l,392.45µS/cm, 165.01mg/l and 19.5mg/l, 15.8mg/l] were estimated to be lower to that of FEPA guideline. Dissolved oxygen (DO) and electrical conductivity (EC), which were not recognized by FEPA standard are [Ewekoro=8.02mg/l, 395.38 µS/cm and Sagamu= 7.5mg/l and 392.45 µS/cm for respectively. Heavy metals as Fe,Zn,Mg,Ca,Cu,Pb,Cd,Mn [Ewekoro=3.92ppm,0.67ppm,19.18ppm,251.8ppm, 0.09ppm,0.5ppm,3.2ppm,and0.05ppm;Sagamu=4.0 2ppm,0.68ppm,19.2ppm,252ppm,0.08ppm, 0.43ppm and 0.44ppm, 2.6ppm] were all below the standard except calcium in both case which can be attributed to the high fraction of calcium in the discharged effluent ; and K (Ewekoro= 187.5ppm and Sagamu= 188ppm)which has no guild with FEPA standards. TDS and EC were further evaluated in order to establish the correlation and the linear relationship***

***between the two cases by analytically preparing the serial solutions of the surface water with deionized water. This concept clearly predicted the status of the surface water samples under the factor of 0.66 as the ratio of TDS to EC at 25oC with a perfect regression (unity) values. The surface water samples were perceived in maintaining their natural states with motion despite the fraction of effluents being discharged in them.***

***Keyword: Chemical industries, effluent, physicochemical parameters***

## 1.INTRODUCTION

The earth surface constitutes the environment of all living things which consist of the atmosphere, hydrosphere, and the lithosphere. The lithosphere is the totality of water bodies while atmosphere is the region of gases which surrounds the earth[1].Environment becomes polluted when it receives or experiences massive discharge of undesirable substances that alter the natural quality of the environment and causing damage to the human, plant, and animal or interferes with the comfort of life[2]. The rapid increase in population and industrialization together with the lack of treatment amenities have resulted in the discharge of toxic chemicals into land, water, and air by man.

In the process, nature's law is distorted and ignored. The basic characteristics of the environment are altered either by removing some essential components such as oxygen or adding undesirable matter into the environment. This will ultimately affect the sustenance of life and normal activities of organism in the ecosystem, which can result in death and extinction of so many species of plant and animals. Waste chemical products from chemical processing industries are very important as they are potential source of pollution. Ogun State, which is part of southwest Nigeria, has vast natural resources like limestone and clay and industrialized potentials. Its extensive limestone deposit according to geographers can last for some five hundred years [3].The multimillion naira cement factory in Sagamu and Ewekoro are the largest cement factory in West Africa. They are even one of the oldest successfully operating cement works in the world according to WAPCO, which was established in 1972 to coordinate cement-based decorative products and became a limited liability company in 1985[4]. Cement manufacturing is a chemical process in which there are two main methods that can be employed [5].Wet Process, which involve the initial blending in the dry state and the crushing of the two primary raw materials (limestone and clay). The mixture is further ground in the raw mills to obtain a fine powder with the addition of water. This raw mill is then fed to a rotary kiln where its sinters at the temperature of about 1400oC to a semi-finish product called clinker. To obtain the end product (Cement), it is pulled and grind in the cement mill. This clinker along with about 3% gypsum are reduced to fine powder and the dry process with limestone and shale are grind together in a mill to form a clay powder called "raw mill". The moisture present is removed by using waste gases from the kiln. The raw mill must be blended to the cement composition and then transferred into kiln where clinker is formed, cooled and 3-5% gypsum is added. Basically, the two processes generate liquid wastes as trade or industrial effluent; as they are directly or indirectly discharged into sewer, surface (groundwater) or on to land. When the raw materials have high alkali or chloride content, a portion of the collected dust must be disposed off as solid waste to avoid alkali buildups. Other materials handling operations such as conveyors result in fugitive emissions. Ambient particulate levels, especially at sizes less than 10 microns have been clearly demonstrated to be related to health impacts [6].Gases especially oxides of nitrogen and sulfur are produced from the reaction of coal gas against sulfur found in the raw materials, while the active alkaline setting can accumulate up to 90 % of the oxides of sulfur [6].Readily available heavy metals within the reactants and in fuels used are directly reacted with the kiln gases. Kilns of cement with their flash point levels can occasionally be employed in the combustion of used organic pollutants can generate secondary pollutants in the name of toxic metals and organics. Pollution generally connotes the introduction of waste materials into the environment and Pollution of water bodies' results when such medium is consciously or otherwise introduced toxic materials of any form into the water. The two sources of effluent discharges are point source in which the harmful substance is released openly into the water body and non-point channel transport wastes indirectly through environmental changes. Water pollution may be traced to four main sources as industrial, domestic, agriculture and environmental pollution.[7] Industrial pollution includes used waters containing chemical compounds and traces elements such as metals and rainwater infiltration through waste disposals, domestic pollution includes rainwater carried through sanitary landfills and accidental breakage of septic tanks and agricultural pollution which may result from rain and irrigation carrying fertilizers, herbicides, and pesticides. Moreover, other factors of water pollution may include domestic runoff and fertilizers with phosphate and nitrates. In high levels, most of the essential nutrients over encourage the development of aquatic organisms while uncontrollable developments of these aquatic organisms conversely block the water channels, reduce the dissolved oxygen by disintegrating and prevent direct light throughout the waters bodies (Eutrophication) [8]. Consequently, this occurrence creates a very toxic and harmful environment to the aquatic organisms. By nature, water bodies experience a process called 'Eutrophication", a phenomenon that gradually transforms the water body with artificial and organic residues [9]. As these deposits penetrate the water bodies, the process of respiration is completely distorted against the aquatic lives, plant development and the depth of the water body becomes limited as the aquatic populace gets suffocated and polluted as towns and villages are often sited near a source of water supply and rivers are used as dumping ground for refuse, human and industrial wastes. The chemical wastes from any industries are emptied into rivers and even when they have not been converted into harmless substances like acids, alkalis, mercury compounds, dangerous metals, total dissolved solids and salts of organic compound. Therefore, this call for a state of emergency with the management and expulsion of wastes being generated by the chemical companies into our immediate ecosystem.

## 2.MATERIALS AND METHODS

All reagents are of Analytical Grade. Temperatures and pHs were conducted in situ with a conventional mercury thermometer and HI9813-5 digital pH meter respectively. Total dissolved solids (TDS) and electrical conductivities (EC) were calculated with mobile HI9813-5 pH, TDS & EC multimeter. Dissolved oxygen was calculated by DO meter. Sulphate was determined by gravimetric method [10], Total Nitrogen and Phosphorus by Ion Chromatography [11] and Mn by Redox Titrimetry [12]. Chloride was by Mohr's method [13] and AAS for the analysis of metals.
(Fe, Zn, K, Mg, Ca, Na, Cu, Pb, Cd, and Mn) [14]

### *2.1. Description of the Study Areas*

Ewekoro is a Local Government Area in Ogun State, Nigeria. Its headquarters are in the town of Itori, at 6°56′00″N 3°13′00″E. It has an area of 594 km² and a population of 55,156 at the 2006 census [15]
The surface water body assessed for this is adjacent to the location of the factory.

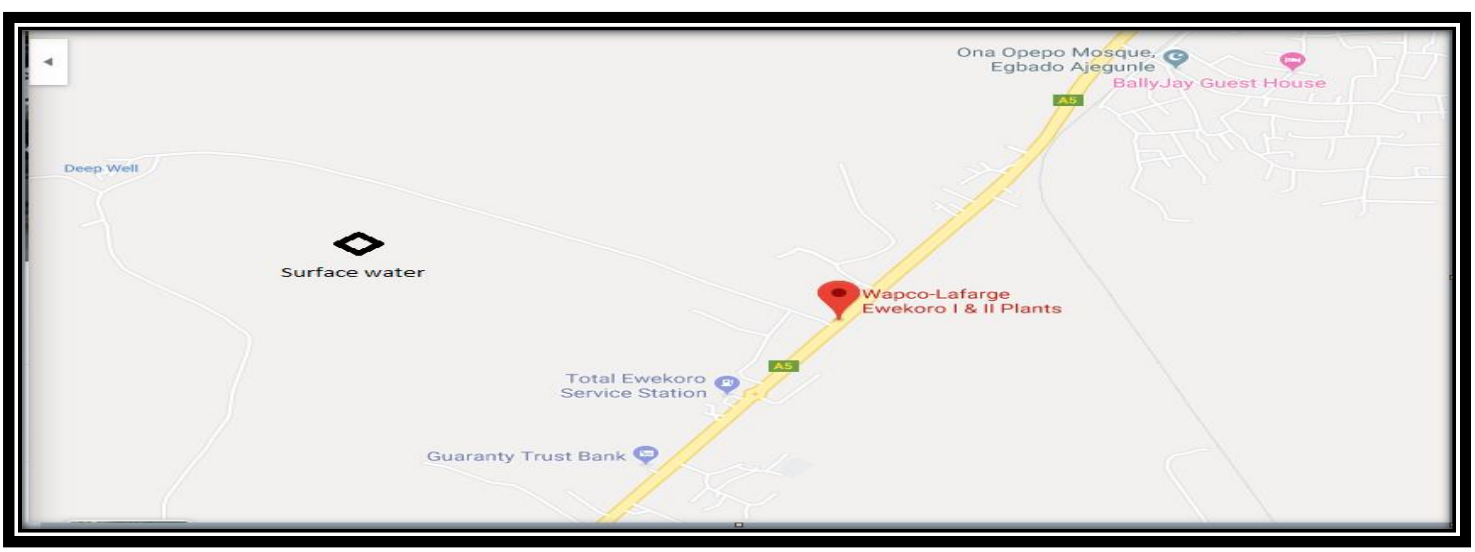


*Figure. 1 Ewekoro Geographical outline*

**Sagamu**

Sagamu or Ishagamu is a town located in Ogun State, near the Ibu River in south-western Nigeria with a Coordinates of 6°50′N 3°39′E. The region is underlain by major deposits of limestone.[16]


*Figure II. Sagamu geographical outline*

### *2.2. Validation and Correlation of Total dissolved solids (TDS) with Electrical Conductivities (EC)*

TDS reflects the activities of inorganic salts and trace quantities of organic matter in water samples while EC is the ability of water to conduct electrical current [17]. Components in TDS and EC can originate naturally from geological activities, seawater, domestic, industrial and agricultural wastes [18, 19]. A couple of regulations governs TDS and EC in water especially on the basis of health, acceptable limit for TDS is between 500 mg/L and 1,000 mg/L and for EC is no more than

1,500 µS/cm [20]. Additional quality standards categorize these parameters with respect to salinity level [21]. TDS has also been classified into four types: Type I is freshwater with TDS < 1,000 mg/L; type II is brackish water with TDS between 1,000 and 10,000 mg/L; type III is saline water with TDS from 10,000 till 100,000 mg/L; and type IV is brine water with TDS > 100,000 mg/L [21].

Hence, water classification based on EC, according to Rhoades (1982) [22,23], is divided into 6 types: type I is non-saline, if EC < 700 µS/cm; type II is slightly saline, if EC rely between 700 and 2,000 µS/cm; type III is moderately saline, if EC higher than 2,000 and less than 10,000 µS/cm; type IV is highly saline with EC value from 10,000 till 25,000 µS/cm; type V is very highly saline, if EC value between 25,000 and 45,000 µS/cm; and type IV is brine water with EC more than 45,000 µS/cm. Meanwhile, these two parameters are correlated and usually expressed by a simple equation:

**TDS = k EC (at 25 0C).**

About 500ml of the two water samples were collected at ten different points on the water bodies and samples for this analysis were prepared in volume per volume with 100ml distilled water (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100v/v).

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September 2019 | Vol. 2 Issue. 4

**Table I. Correlation EC and TDS in various type of water**

| EC in 25 $^0$C | Ratio TDS/EC (k) | Source |
|---|---|---|
| Natural water for irrigation | 0.55 - 0.75 | [14] |
| Natural water, EC = 500 – 3,000 $^{\mu S}/_{cm}$ | 0.55 – 0.75 | [9] |
| Distillate water, EC = 1 – 10 $^{\mu S}/_{cm}$ | 0.5 | [15] |
| Freshwater, EC = 300 – 800 $^{\mu S}/_{cm}$ | 0.55 | |
| Seawater, EC = 45,000 – 60,000 $^{\mu S}/_{cm}$ | 0.7 | |
| Brine water, EC = 65,000 – 85,000 $^{\mu S}/_{cm}$ | 0.75 | |

## 3.RESULTS AND DISCUSSION

**Table II .Physico-Chemical parameters conducted on the two surface waters**

| Physico-Chemical parameters | Ewekoro | Sagamu | FEPA Standard |
|---|---|---|---|
| Temperature(°C) | 30 | 40 | < 40 |
| pH | 7.60 | 7.70 | 6-9 |
| Dissolved Oxygen (mg/l) | 8.02 | 7.50 | NG |
| Biological oxygen demand at 20°C (mg/l) | 7.67 | 8.99 | 50 |
| Total dissolved solids (mg/l) | 257.00 | 255.09 | 2000 |
| Electrical Conductivity (µS/cm) | 395.38 | 392.45 | NG |
| Nitrate (mg/l) | 16.30 | 15.80 | 20 |
| Phosphate (mg/l) | 4.86 | 4.03 | 5 |
| Sulphate (mg/l) | 166.03 | 165.01 | 500 |
| Chloride (mg/l) | 15.50 | 19.50 | 600 |

*Figur Figure II. 2D chart of heavy metals distribution of the two case studies (Sagamu and Ewekoro)*

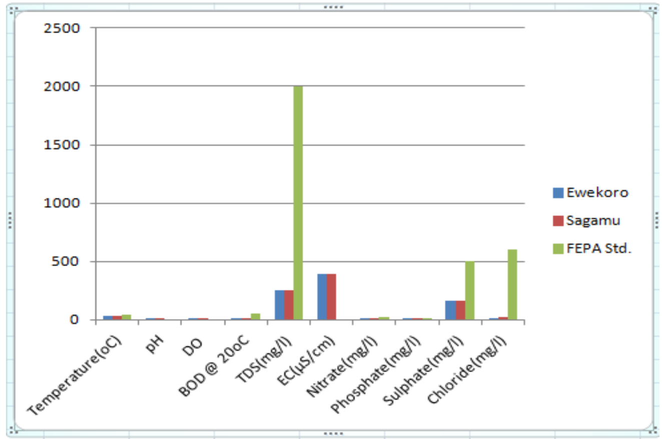
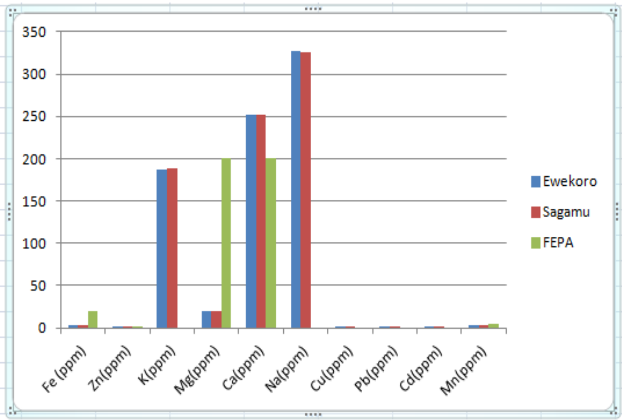



*Figure I. 2D column chart for the physicochemical characteristics of the two case studies (Sagamu and Ewekoro)*

**Table III. Heavy metal analysis**

| Heavy Metal | Ewekoro | Sagamu | FEPA Standard |
|---|---|---|---|
| Fe | 3.92 | 4.02 | 20.00 |
| Zn | 0.67 | 0.68 | 0.10 |
| K | 187.50 | 188.00 | NG |
| Mg | 19.18 | 19.20 | 200 |
| Ca | 251.80 | 252.00 | 200 |
| Na | 326.50 | 325.00 | NG |
| Cu | 0.09 | 0.08 | < 1 |
| Pb | 0.50 | 0.43 | < 1 |
| Cd | 0.05 | 0.44 | < 1 |
| Mn | 3.20 | 2.60 | 5.00 |




*Figur  Figure II. 2D chart of heavy metals distribution of the  two case studies (Sagamu and Ewekoro)*

**Table III. Electrical conductivities and Total dissolved solids of the two case studies (Ewekoro and Sagamu)**

| Water sample's concentration (per100mldeionized water) | Ewekoro | | Sagamu | |
|---|---|---|---|---|
| | EC (µS/cm) | TDS (mg/l) | EC (µS/cm) | TDS (mg/l) |
| 10 | 160.61 | 106 | 154.55 | 102 |
| 20 | 195.46 | 129 | 203.03 | 134 |
| 30 | 227.28 | 150 | 253.03 | 167 |
| 40 | 271.21 | 179 | 296.10 | 196 |
| 50 | 304.55 | 201 | 348.49 | 230 |
| 60 | 348.49 | 230 | 393.94 | 260 |
| 70 | 384.85 | 254 | 442.42 | 292 |
| 80 | 422.73 | 279 | 492.42 | 325 |
| 90 | 462.12 | 305 | 539.39 | 356 |
| 100 | 500.00 | 330 | 592.42 | 391 |

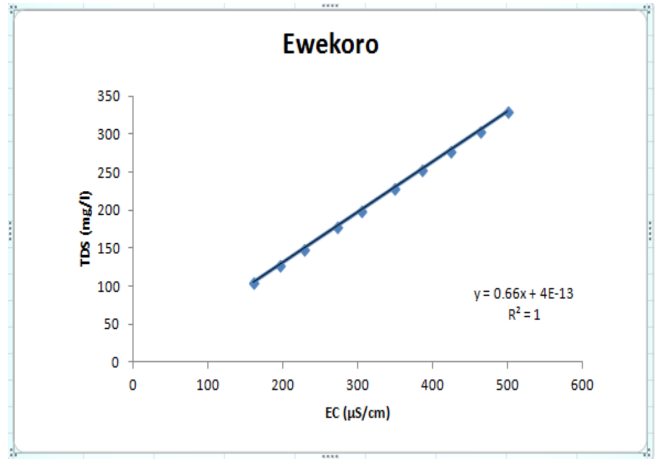



*Figure III. Linear plot of TDS and EC for Ewekoro's case*

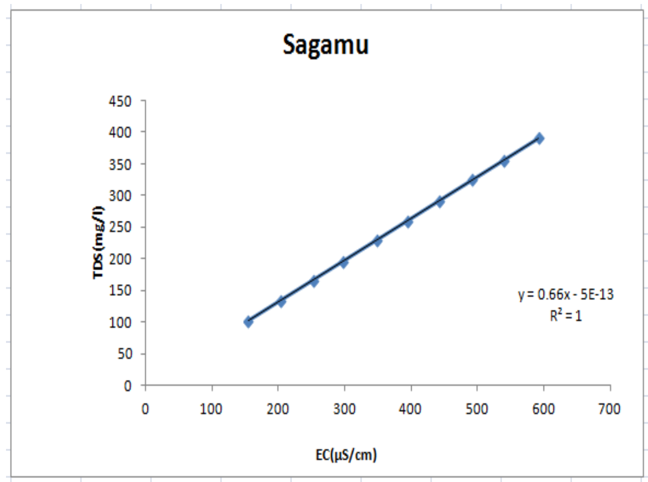



*Figure IV. Linear plot of TDS and EC for Sagamu's Case*

## 4.DISCUSSION

Table II and figure I disclosed the in-situ temperatures of the two cases to be below the FEPA standard which should not be more than 40oC and 15 meters from the point of effluent release. Technically, it can be asserted that the atmospheric or the ambient temperature at the period of sampling and analysis is the function of the surface water temperature gradients and other temperature sensitive parameters. The pH of sagamu surface water which was more alkaline (9.0) to that of Ewekoro (7.6) was also of FEPA standard (9.0). Biological oxygen demand at 20oC for the two cases [Ewekoro=7.67mg/l and Sagamu=8.99mg/l] still declares that biological decompositions of organic matters are constantly in the process preventing organic matter overpopulation and stress within the aquatic environment. Total dissolved solids [Ewekoro= 257mg/l and Sagamu=255.09mg/l] which are indications to the degree of salinities within the aquatic environment and lower to that of FEPA standard of 2000mg/l.

Electrical conductivities [Ewekoro= 395.38μS/cm and Sagamu=392.45μS/cm] expresses the potentials of the two aquatic systems with the capacity for conduction of an electric charge with respect to ion concentration, ionic strengths, and the temperature. [24].

Sulfates in both cases [Ewekoro= 166.03mg/l and Sagamu= 165.01mg/l] against 500mg/l with FEPA standard are still acceptable against the higher magnitude above FEPA limit that can induce laxative effect, diarrhea and corrosion on plumbing materials (copper piping).[25]

Chlorides are [Ewekoro= 15.5mg/l and Sagamu= 19.5mg/l] and below the standard of 600mg/l with FEPA. They generally react with sodium, magnesium, and calcium forming respective salts of calcium and can be toxic at high doses.[26].

Nitrate [Ewekoro=16.3mg/l and Sagamu= 15.8mg/l] are bellowed the standard [FEPA=20mg/l] because at high concentration can trigger conditions that can interfere with the capability of the red blood cell to transport oxygen [27]. Most sources of excessive nitrates come from domestic, industrial and agricultural activities. Dissolved oxygen was estimated to be 8.02mg/l and 7.59mg/l for Ewekoro and Sagamu respectively. This is one of the most important indicators of water quality which is very essential to the survival of all aquatic organisms (fauna and flora).

Heavy metals such as Iron (Fe), Zinc (Zn), Magnesium (Mg), Calcium (Ca), Copper (Cu), lead (Pb), Cadmium(Cd) and manganese (Mn) in both cases are [Ewekoro = 3.92,0.62,19.18,251.8,0.09,0.5,0.05 and 3.2mg/l ;Sagamu=4.02,0.68,19.2,252,0.08,0.43,0.44 and 2.6mg/l] .They are all below the FEPA standards except potassium and sodium that have no guidelines with FEPA. The major threats out of these heavy metals rest on lead and cadmium as they pose acute effects above the limit (< 1mg/l).

Furthermore, total dissolved solids and electrical conductivities have been related parameters that clearly define the ionic activity as the function of salinity levels with the same water samples. The ratios of TDS to EC as estimated in table III established and predicted the nature or status of the water samples under study as categorized in table I above and Figure III and IV. The relationship between the two parameters (TDS and EC) is observed to be linear with correlations of 1(unity)

## 5.CONCLUSION

Accepting and believing that most important phenomena in life are air, water, and soil and as any imbalance or distortion would obviously shut down our existence in this part of the universe. Cement effluents released into the surface water bodies is no exception to what can trigger such dangers. Meanwhile with this study, the surface water in both cases was observed in maintaining their natural flow and conditions by virtue of TDS and EC relationship (0.66) pattern which is an advantage against the accumulations of cement by-products pollutants. Location of any chemical industries within a city, town, villages or any settlements is generally motivated by the proximity, presence and natural availability of raw materials for such industry. However, the aspect of pollution prevention has always been ignored. Hence, there should be some strategic mechanisms from estate or regional managers and pollution control organizations like Federal Environmental Protection Agency, public analyst of Nigeria and other relevant stakeholders to team up and ensure that industrial wastes in any form are controlled by conversion into less toxic forms or products.

## 6.RECOMMENDATION

The effects and impact of different time zones that will factor different ambient temperature should be evaluated and with other types of chemical industries with effluent wastes at different locations within the country

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