STUDY OF THE PHYSICO-CHEMICAL CHARACTERISTICS OF INDUSTRIAL EFFLUENTS FROM A BREWERY INDUSTRY IN OGUN STATE, NIGERIA

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ABSTRACT
Water plays an important role in the life of human beings. In the last few decades, limitless urbanization has caused a serious pollution problem due to the disposal of sewage to the water bodies. This study investigates the level of wastewater pollution by analyzing its chemical characteristics at five wastewater collectors. In this investigation physico-chemical parameters such as colour, temperature, total alkalinity, chloride, total hardness, total suspended solid, pH, dissolved oxygen and heavy metal determination using Atomic Absorption Spectrophotometer (AAS). Experimental results show that the concentration levels of the some parameters does not conform to the guide line stipulated by Federal Environmental Protection Agency (FEPA). Concentration ranges as follows: temperature (45-33^{o}C), pH (11.24-9.15), Total Alkalinity (1500-190mg/L), Total suspended solid (39.6-38.3mg/L). Chloride and total hardness conformed to FEPA standards with their respective range of values (82-30mg/L), and (80-110mg/L). Dissolved oxygen (2.0-3.4mg/L) fall below standard. The trace metals concentration range as follows: Iron (23.5-24.1mg/L), Cu (0.26-0.24), Zn (2.24mg/L) and Cd (0.00), Iron and zinc fall beyond FEPA standard which are 20.0 and 0.1mg/L respectively while copper conform with the standard. Cadmium is not detectable.

Keywords: Effluent, Physicochemical, Heavy Metals and Brewery.

1. INTRODUCTION

Industrialization is an important tool for the development of any nation. Consequently, the industrial activity has expanded so much all over the world. Today, it has become a matter of major concern in the deterioration of the environment (Nivruti *et al.*, 2013). Water is one of the most valuable natural resource for all living creatures on the earth and essential for the sustenance of life as exemplified by its diversified uses such as drinking, cooking, washing, irrigation, farming, industrial activities etc. Water may be contaminated by various means that may be chemically or biologically and may become unfit for drinking and other uses. Domestic wastewater contains a large amount of organic matter, nitrate, phosphate, detergents, inorganic salt, oil etc. (Rathore *et al*., 2014).

Pollution from industrial disposal and effluent discharges is becoming a serious environmental issue in many developing countries of Africa (Uzoukwu *et al*., 2004). The use of dams polluted by industrial effluents from textiles, shoes, cosmetics, plastics, and other household industrial consumables has its negative consequence on the plants through the alteration of the physico-chemical properties of the receiving water body. The aquatic habitats are killed by the toxic chemicals with the resultant disruption of the aquatic ecosystem and its food chain. The decomposition of the organic materials by micro-organisms in the aquatic ecosystem leads to the lowering of the level of dissolved oxygen, which in turn inhibits the growth or cause the death of the aquatic habitats (Onuegbu, 2008). The biochemical oxidation of the natural and the industrial wastewater can be represented by the following equation: Oxidizable material + bacteria + nutrient + $O_2 \rightarrow CO_2 + H_2O$ + oxidized inorganic(s) (Aleksandar *et al.,* 2011)

There is therefore every need to carry out a research to find out the elements and compounds present in the effluents of Brewery industries. The results of the analysis of these effluents will reveal the presence and concentrations of these pollutants. The contents and their concentrations will be compared with a reference standard and if found to be unsafe, recommendations will be made on the proper way of disposing the effluent such that it will not be harmful to life (Adriano, 2001).

The term effluent can be defined as liquid waste flowing out of a factory, farm, commercial establishment, or a household into a water body such as a river, lake, or lagoon. In various under-developed countries, untreated sewage and industrial effluents are utilized for the cultivation of crops and vegetables. It is a common practice in Nigeria where farmers suppose it to be a source of irrigation and nutrients for cultivation while administrators assume it as a low cost method of disposal (Ahmed, 2000 Ahmad, *et al*. 2003).

The aim of this study is to analyze the physicochemical compounds and heavy metal concentrations in the effluents generated by a brewery industry in Ogun state, Nigeria. The results from the analyses will be compared with reference standards to ascertain its compliance with regulatory standards.

2. MATERIALS AND METHODS

2.1 Collection of Sample

The effluent samples were collected from the 3 different points of discharge of the company; the source of effluent, the middle course and point of discharge into the municipal drain. The samples for the dissolved oxygen were collected in 300ml BOD bottles avoiding contact with air and fixed on the spot, while samples for the physicochemical parameters were collected with plastic bottles pre-cleaned by washing with non-ionic detergents and rinsed with tap water.

2.2 Physicochemical Analysis

All field meters and equipment were checked and calibrated according to the manufacturer's specification. pH, temperature, transparency and depth were determined while on site. Other parameters including heavy metals were analyzed in the laboratory.

2.3 Determination of pH

Method: pH was measured by electrometric method using laboratory pH meter model 31500 (expressway).
Procedure
The electrodes were rinsed with distilled water and blot dry. The pH electrodes were then rinsed a small beaker with a portion of the sample. Sufficient amount the sample was poured into a small beaker to allow the tips of the electrodes to be immersed to a depth of about 2cm. The electrode was at least 1cm away from the sides and bottom of the beaker. The temperature adjustment dial was set accordingly.
The pH meter was turned on and the pH of the sample recorded.

2.4 Determination of Water Hardness

Method: Hardness was measured using standard analytical method of APHA.
Procedure
50cm3of the water sample was introduced into a beaker and 1cm3 buffer solution of NH3 added. Three drops of solocrome Black T indicator was also added and the solution swirled properly. The mixture was titrated with 0.01 EDTA solution until it changed from wine red to pure blue with no bluish tinge remaining. The total hardness of the water sample was calculated.

$$\text{Total hardness CaCO3 mg/L} = \frac{\text{Volume of titrant} \times 100}{\text{Volume of sample (ml)}}$$

2.5 Determination of Chloride

Method: Chloride was analyzed according to APHA standard method.

Procedure
A 100ml of the clear sample was pipetted into an Erlenmeyer flask and the pH adjusted to 7-10 with either H2SO4 or NaOH solution. Then 100ml of K2CrO4 indicator solution was added with standard solution of AgNO3 in a permanent reddish brown coloration. The AgNO3 titrant was standardized and a reagent blank established. A blank of 0.2-0.3ml was usually used.
Calculation;
Chloride concentration = Titre value (x) × 10 = 10xmg/l.

2.6 Determination of total alkalinity

Method: Hardness was measured using standard analytical method of APHA

Procedure

100ml of the waste water sample was place transferred into a conical flask 2drops of phenolphthalein indicator was added and then titrated with the standard HCl until the pink colour just disappears. The titre value was noted as phenolphthalein at point (p).

To the above solution 3 drops of methyl orange indicator was added and the titration is continued until a sharp color change from yellow to red took place. The total titre value from the beginning of the experiment is recorded as methyl orange end – point M.

Calculation

2(P) = CO_{3-} and (M) – 2(P) should correspond to HCO_{3-} .

This value of N/50 HCl equivalent to $HC0_{3-}$ = (M) – 2(P)

2.7 Determination of dissolved oxygen

Method: Hardness was measured using standard analytical method of APHA

Procedure

The water is collected in a 300ml BOD bottle avoiding contact with air. 2ml of $MnSO_4$ and 2ml of alkaline iodide azide reagent were added in such a way that the tip of the pipette should dip below the liquid surface while adding the reagent. The bottle is stoppered and mixed by inverting the bottle 3-4 times. 1ml of conc. H_2SO_4 was added and mixed well till the precipitate went into solution.

230ml of the clear solution is measured into a conical flask and titrated against standard sodium thiosulphate solution using starch as indicator toward the end point.

NOTE: 203ml taken for titration will correspond to 200ml of the original sample. This is to allow for correction to 2ml $MnSO_4$ and 2ml alkali iodide-azide reagent.

$\frac{200 \times 300}{300-4}$ = 203ml

Calculation

1ml of 0.05M $Na_2S_2O_3$ = 2mg of DO/ litre

xMl of 0.05M $Na_2S_2O_3$ = X x 2mg of DO/litre

2.8 Determination of total suspended solids

Method: Hardness was measured using standard analytical method of APHA

Procedure

100ml of water samples was accurately measured into 250ml evaporating dish and transferred to the stream bath. Evaporated to dryness and dried at 105^0C for 1hour in the oven. It was then cooled in the desiccator and weighed. The change in weight from the original weight of a cleared empty evaporating dish pre-ignited and cooled and noted.

Calculation

Total solids (mg/L) = $\frac{(X-Y)\times 1000\times 1000}{Volume\ of\ sample\ (ml)}$

X = Weight of sample and evaporating dish

Y = Weight of empty evaporating dish

2.9 Determination of temperature

Method: Hardness was measured using standard analytical method of APHA

Procedure

Temperature was measured in-situ on the body of the waste water by the use of mercury in glass thermometer. The bulb of the thermometer was dipped inside the water and the reading was taken when the mercury thread become stable. The unit is in degree centigrade.

2.10 Determination of metals

Sample preparation

The method used is instrumental method;

200ml of well mixed sample solution was measured into a clean 250ml evaporating dish. 2ml of concentrated nitric acid was introduced into the sample solution and was evaporated on the water bath to less than 20ml. The digested sample was further made to 20ml. The digested sample was further made to 20ml mark and stored in pre-cleaned 50ml syrup bottles for analyses. This procedure was procedure was repeated for the blank but with distilled water. The metal content was determined by Perkin Elmer Atomic spectrophotometer metals determined by Perkin Elmer AAS include Fe, Cu, Zn and Cd.

3. RESULTS AND DISCUSSION

This study shows the comparative analyses of physicochemical parameter of wastewater from Sona breweries were. The physicochemical parameters under study were the temperature, pH, TSS, total hardness, total alkalinity, dissolved oxygen and Chloride. The physico-chemical parameters of the effluents investigated are presented in Table 1.

3.1 Water Temperature

In the present study the water temperature ranged from $33^{O}C$ to $45^{O}C$, although there was a light shower during the collection sample which was done at around 12 noon. The temperature at the first point ($45^{O}C$) is a bit higher than the FEPA 1991 standard $< 40^{O}C$ while the other values conform to it. Temperature is one of the most significant factors that affect the aquatic environment (Weqar *et al*., 2012). Hariharan (2010) reports that bio-chemical reactions of aquatic organisms are temperature dependent. Increase in temperature of water body will promote chemical reactions in the water.

3.2 pH

pH is the hydrogen ion activity and a measure of acidity and alkalinity in aquatic bodies. pH is one of the important biotic factors that serves as index for pollution (Sagar *et al.,* 2012). The pH values range from 11.24 to 9.15 which is higher than the FEPA standard. The water is too basic which could be attributed to high concentration of carbonates in the water. The principal component regulating ion pH in natural waters is the carbonate, which comprises CO_2, H_2CO_3, and HCO_3 (Kataria *et al.,* 1996).

3.3 Hardness

The hardness of water is not the chemical parameters but indicates the water quality mainly in terms of Ca and Mg and expressed as $CaCO_3$. The hardness has no known adverse effect. It is property of water of which prevents the lather formation with the soap (Tekade *et al.,* 2011). Water containing $CaCO_3$ at low concentrations below 60mg/L is generally considered as soft; 60-120mg/L is moderately hard; 120-180mg/l is hard; and more than 180mg/l is very hard (McGowan, 2000). The water hardness ranges from 80-110mg/L and therefore can be categorized as moderately hard water and can be removed by boiling.

3.4 Alkalinity

High alkalinity is a measure of wastewater strength. It shows the capacity of wastewaters to neutralize acids, and is undesirable. The alkalinity of water may be caused due to OH^-, CO_3^{2-}, HCO_3 ions. Alkalinity is the estimate of ability of water to resist change in pH upon addition of acid (Tekade *et al.,* 2011). The alkalinity of the water reduced from the point source to the gate.

The high value of alkalinity indicates the presence of major sources of CO_3^{2-} from the acid used to clean and disinfect brewery. The situation which is undesirable for intended use of water.

3.5 Chloride

The presence of chloride in natural water can be attributed to the salt deposits, discharge of effluents from chemical industries, sewage discharges etc. Each of these sources may cause the local contamination of both surface and ground water (Tekade *et al.,* 2011). Chloride content in the studied effluent was found to be between 30mg/L to 82mg/L. This level of chloride content is below the FEPA standards.

3.6 Dissolved Oxygen

Dissolved oxygen is of significant importance to the respiration activities of the aquatic organisms and effluents with very low DO may have a negative impact on the sustainability of the rivers in the basin (Tekade *et al.,* 2011). The DO values increases from point 1to point 3 ranging from 2.0mg/L-3.4mg/L which is very low hence a lot of oxygen has been used up. The presence of free oxygen in water is an indication of the ability of that water to support biological life. Low value of DO may be due to higher water temperature and increased activity of microorganisms in the water which consumes a lot of oxygen due to metabolic process and the decomposition of organic material (Sahni *et al.*, 2012). Decrease in DO will lead to increases in BOD and COD values (Siyanbola, *et al.*, 2011)

3.7 Total Suspended Solids

Total dissolved solids are a measure of total inorganic substances dissolved in water. The total suspended solids affect the light intensity of water; suspended solids are the cause of suspended particle inside the water body influencing turbidity and transparency (Tekade *et al*., 2011). Total suspended solids content in this study was found to be between 39.6mg/L to 38.1mg/L. This level of chloride content is below the FEPA standards.

Table 1: Physico-chemical characterization of industrial effluents analyzed

Effluent Points	Temp (^{O}C)	pH	Total Hardness (mg/L)	Total Alkalinity (mg/L)	Chloride (mg/L)	Dissolved Oxygen (mg/L)	Total Suspended Solids (mg/L)
Point 1	45	11.24	80	1500	82	2.0	39.6
Point 2	38	9.88	90	460	42	2.4	38.1
Point 3	33	9.15	110	190	30	3.4	28.3

This study shows the comparative analyses of the concentration of metals of the effluent from Sona breweries. The metals studied include iron (Fe), copper (Cu), zinc (Zn) and cadmium (Cd). Table 2 shows the concentration of metals from the various effluent points.

Iron (Fe) metal concentration values ranges from 23.0mg/L-24.1mg/L which is higher than the FEPA (1991) recommended concentration level (20mg/L). Zinc (Zn) however at the first point has a higher concentration value (2.24mg/L) which is higher than the FEPA (1991) recommended level (<1), which can be attributed to wort which is a major raw material in beer productions and could also be attributed to Zn used in electroplating storage materials and boilers. All the other points conform to the FEPA (1991) level.

Copper (Cu) values ranges from 0.24mg/L- 0.26mg/L which falls between the FEPA (1991) limit. Cadmium (Cd) shows insignificant contribution in the effluent as it was not detected. Matsuo *et al*. (1995) report that high concentration of Cadmium inhibits bio-uptake of Phosphorus and Potassium by the plants.

Table 2: The concentration of metals in the effluents analyzed

Effluent Points	Fe (mg/L)	Cu (mg/L)	Zn (mg/L)	Cd (mg/L)
Point 1	23.5	0.26	2.24	ND
Point 2	23.0	0.24	0.24	ND

Point 3	24.1	0.25	0.24	ND

ND: Not Detected

4. CONCLUSION

This study has shown that the brewery industry discharge effluents with high degree of alkalinity value which are not in compliance with FEPA set standards. This questions the functionality of the treatment plants in this company. Should these companies continue to discharge untreated wastes into the environment thereby building up in the metal concentrations of the water bodies and which may pose serious threat to both the aquatic habitat and human beings that consume these aquatic animals? Strict environmental laws become imperative so as to curb this stress.

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