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Physicochemical and Elemental Properties of the Discharged Wastewater from a Brewery Industry Located In Northwest Nigeria

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Abstract: *Physicochemical and elemental analyses were conducted on the discharged wastewater of a brewery industry located in Northwest Nigeria. Samples of the wastewater were collected from the discharge point and analyzed using standard methods. The physicochemical parameters analyzed and their corresponding mean values are shown as follows; pH 7.87, Temperature 33.05°C, Turbidity 156.50NTU, Electrical conductivity (EC) 2135.00µs/cm, Total Dissolved Solutes (TDS) 495.00mg/L, Dissolved Oxygen (DO) 2.83mg/L, Biological Oxygen Demand (BOD) 75.75mg/L, Chemical Oxygen Demand (COD) 480mg/L, Nitrate 2.55mg/L, Sulphate 55.50mg/L and Phosphate 40.00mg/L. Also, five elements where analysed for their presence in the wastewater and the mean values obtained are given as; Chromium 0.399 mg/L, Nickel 0.748mg/L, Zinc 1.215mg/L, Cadmium 0.175mg/L and Lead 1.700mg/L . These results obtained were compared to the given standards by National Environmental and Sanitation Regulatory Agency (NESREA) and World Health Organization (WHO).It was observed that the results obtained were within the permissible limits (NESREA and WHO) except for Electrical conductivity (EC), Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Turbidity, Phosphates, Cadmium and Lead which exceeded the given limits.*

Keywords: *NESREA, physicochemical, phytochemical, wastewater and WHO*

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I. Introduction

Industrialization has become an important factor to the development of every country's economy, through the establishment of plants and factories. However, the waste or by-products discharged from them (if untreated) are severely disastrous to the environment because it consists of various kinds of contaminant which contaminates the surface water, ground water and soil. This is a great burden in terms of wastewater management and can consequently lead to a point-source pollution problem, which not only increases treatment cost considerably, but also introduces a wide range of chemical pollutants and microbial contaminants to water sources [1]. For instance, in areas where industrial waste effluents are discharged into surface waters, there is a general reduction in the quality of such water and its ability to support aquatic life is equally reduced.

A brewery is a dedicated building for the making of beer, though beer can be made at home, and has been for much of beer's history [2]. The diversity of size in breweries is matched by the diversity of processes, degrees of automation, and kinds of beer produced in breweries. The brewery industries in Nigeria are one of the flagship consumer sectors and have rightly become a priority holding for many investors in the Nigerian Stock Market [3]. Brewery industries have been known to cause pollution by discharging effluent into receiving stream, ground water and soil .These industries generate wastewater which is sometimes discharged untreated into the environment and they flow into inland water bodies resulting to stench, discoloration and a greasy oily nature of such water bodies [4].

Production steps in the brewery processes include malt production, wort production and beer production [5]. Water consumption for breweries generally ranges from 4-8 cubic meters per cubic meter of beer produced. The pollution discharge from brewery plant effluent comes from the losses in the beer production process and from the clean-in-place (CIP) system located in the brewing house, cellar house and bottling house. The quality of brewery effluent can fluctuate significantly as it depends on various different processes that take place within the brewery. The organic components in brewery effluent are generally easily biodegradable since these mainly consists of sugars, soluble starch, ethanol, volatile fatty acids as well as solids which are mainly spent grains, waste yeast and trub [6]. Thus, based on their properties, the constituents of brewery effluent fluid

can be classified as: physical, chemical and biological. The physical characteristics of the effluent fluids constitute the total solids content, smell or odour, colour and temperature. The important chemical characteristics of effluent fluid are determined by the pH value, chloride content, nitrogen, fat and grease content, dissolved oxygen, chemical oxygen demand and biochemical oxygen demand. The biological characteristics relate to the various micro-organisms found in effluent fluid, some of which may be pathogenic.
There are regulatory bodies guiding the disposal of industrial effluent into the environment. These bodies include NESREA, WHO, USEPA, EU, e.t.c. The standard provision by National Environmental and Sanitation Regulatory Agency (NESREA) in Nigeria for some Brewery wastewater parameters are as follows; pH 6.0-9.0, Temperature ,40^{o}C,TSS 650mg/l, TDS 2100mg/l, BOD 30mg/l, COD 250mg/l, Oil and grease 10-100mg/l, Zn <1.00mg/l, Pb 0.1-1mg/l, Cd <0.1mg/L, Hg 0.01mg/l, Ammonical Nitrogen 50mg/l, e.t.c [7].

II. Materials And Method

2.1.0 Materials

The materials used in this research were sourced from Sabon-gari market and National Research Institute for Chemical Technology Laboratories both in Zaria. The equipments used are properties of National Research Institute for Chemical Technology Laboratories. The chemicals used for this Research were of analytical quality.

2.2.0 Study Area

The site for this research was a Brewery industry located in the Northwestern part of Nigeria. It is marked by distinct wet and dry season. It has high temperature all year round. The mean daily temperature in the area can be as high as 34^{o}C between months of March and May. Temperature could be as low as 20^{o}C during the December to January. This low temperature is intensified by humidity due to the dry harmattan wind [8].

2.3.0 Sampling Points and collections

The wastewater samples were collected at the point of discharge from the brewery industry. Ten (10) liters of clean gallons were pretreated with nitric acid before proceeding to the sampling site for sample collection. At the sampling site, the sampling containers were rinsed with the effluent samples three times and then filled to the brim. Collection was done in replicate and pooled with their covers replaced, labeled and kept in the ice pack to retain its original microbial activities. The samples were then transported to the Laboratory immediately and stored in the refrigerator at about 4°C prior to analysis.

2.4.0 Analysis

The physicochemical and elemental analyses were conducted at the Industrial and Environmental Technology department (IETD) Laboratory of National Research Institute for Chemical Technology Zaria.
2.4.1.0 Determination of the Physico-Chemical Parameters of the Discharged Brewery Wastewater Samples

2.4.1.1 pH, Temperature, Conductivity and Total Dissolved Solutes

Prior to the collection of samples, the following parameters were analyzed at each point of sampling. The pH, temperature, conductivity and total dissolved solutes of the effluent samples were determined at the point of sampling using HANNA instrument model 191300 with strict adherence to the procedure for analysis as stipulated in the instruction manual. The electrode was rinsed thoroughly in distilled water and immersed into each sample, readings were taken and recorded. The device was switched to each specific parameter to be analyzed before the reading was observed.

2.4.1.2 Determination of Dissolved Oxygen and Biochemical Oxygen Demand.

The Modified Winkler- Azide Method was used to analyse the brewery effluent samples for dissolved oxygen (DO) while Biochemical oxygen demand (BOD_5) was determined by the difference between DO of samples immediately after collection and DO of samples after incubation at 20ºC for five days [9].Biochemical oxygen demand is measured by the volume of oxygen required by the organisms to metabolize it under aerobic conditions. The DO was assayed by determining the dissolved oxygen content using the Alkaline – Azide modification of Winkler's method [7]. Each brewery wastewater dilution was poured into two 300ml bottles labeled Day 1 and Day 5. Two milliliters (2mL) $MnSO_4$ and alkali-iodide-azide reagent was added well below the surface of the liquid and stoppered with care to avoid the formation of bubbles. The solution was mixed by inverting the bottle a number of times until clear supernatant water was obtained. The solution was allowed to settle for about 2 min, the dissolved oxygen (DO) content of the sample labeled Day 1 was determined immediately while after which 2ml of concentrated H_2SO_4 was added by allowing the acid to run down the neck of the bottle. The bottle was stoppered again and mixed by inverting gently until dissolution is complete. When the iodine is uniformly distributed, 203mL of the sample was taken. Two milliliters (2mL) of starch solution was added and was titrated using 0.0125 M Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) solution drop wise until the blue color disappears to a colorless solution. The other sample labeled Day 5 was kept in an incubator at 20^0C for five days before determination of the dissolved oxygen content. The BOD (mg/L) was obtained by finding the difference between the DO of the first day and fifth day.

2.4.1.3 Determination of Chemical Oxygen Demand

This was determined using the titrimetric method [10]. Anti-bumping granules were introduced into a reflux flask. Twenty milliliters (20ml) of the sample was measured into the refluxing flask and 2ml of 20% m/V mercuric sulphate solution was added and swirled. Ten milliliters (10ml) of 0.021M potassium dichromate was added to the mixture. Using a dispensing pipette, 30ml of concentrated sulphuric acid containing silver sulphate was also added. The contents in the flask was fitted to a condenser and refluxed for 1 hour. After 1 hour, the flask was removed and allowed to cool for approximately 10 minutes. The condenser was washed with distilled water and then the content of the flask was diluted to 100ml.Two drops of Ferroin indicator was added to the content in the flask and the residual dichromate was titrated with standardized ferrous ammonium sulphate. The COD was obtained using equation 1 below

: COD mg/l = (Vb - Va) x 8000 x M/volume of sample

Where,

V_b = average number of ml ferrous ammonium sulphate used in titrating the appropriate blank.

V_a = number of ml ferrous ammonium sulphate used in titrating the sample.

M = Molarity of standard ferrous ammonium sulphate solution.

2.4.1.4 Determination of Turbidity

This was done using the Hach Model 2100P ISO portable Turbidimeter. Turbidity is based on the comparison of the intensity of light scattered by the sample under defined conditions with the intensity of the light scattered by a standard reference suspension under the same conditions. The Turbidimeter used for this study measures within the range of 0.01-9.99 NTU. To the sample cell, 0.1ml of brewery sample was added and made up to 10ml with distilled water, the body of the cell was wiped gently with soft tissue and placed in the turbidity meter such that the vertical mark coincides with the mark in the meter and then covered. The reading was taken when a stable value was observed. The results of the analysis were multiplied by 100.

2.4.1.5 Determination of Nitrate

Nitrate content was measured in the laboratory using Wagtech photometer model 7100.The nitratest tube was filled to the 20ml mark. One level spoonful of nitratest powder and one nitratest tablet was then added. The screw cap was replaced and shaken to obtain a homogenous mixture. The tube was allowed to stand for about one minute and then inverted three or four times to aid flocculation. The tube was then allowed to stand for two or four minutes to ensure complete settlement. The screw cap removed and test tube cleaned with tissue. 10ml of the clear solution was decanted into the test tubes. One nitricol tablet crushed and added into the tube. The tube was then allowed to stand for ten minutes for full color development. The solution was read using photometer at a wavelength of 570nm.

2.4.1.6 Determination of Sulphate

Sulfaver 4 Method was used to analyze the wastewater samples for Sulphate (SO_4^{2-}) content. Sulphate ions in the sample react with barium in the sulfate 4 and form a precipitate of barium sulphate. The amount of turbidity formed is proportional to the sulphate concentration. The sulfaver 4 also contains a stabilizing agent to hold the precipitate in suspension. Test result was measured at 450nm using HACH DR2400 portable spectrophotometer [9].

2.4.1.7 Determination of Phosphate

Phosphate content of the brewery wastewater was measured in the laboratory using Wagtech photometer Model 7100. PhosVer® 3 (ascorbic acid) method was used to analyze the wastewater samples for phosphate (PO_4^{3-}) content. Phosphates react with molybdate in an acid to produce a mixed phosphate/ molybdate complex. Ascorbic acid then reduces the complex giving an intense molybdenum blue colour. Test result was measured at 880nm using HACH DR 2400 spectrophotometer [9].

2.4.1.8 Determination of Metals in the Brewery Wastewater Samples

The brewery wastewater samples were digested as follows; 100 ml of the sample was transferred into a beaker and 5mL concentrated HNO_3 added. The beaker with the content was placed on a hot plate and evaporated down to about 20ml then cooled and another 5ml concentrated HNO_3 was also added. The beaker was reheated as a small portion of HNO_3 was added until the solution appears light colored and clear. The beaker wall was washed with distilled water and the sample filtered to remove some insoluble materials that could clog the atomizer. The volume was adjusted to 100ml with distilled water [10]. Chromium, Lead, Zinc and Cadmium concentrations in the digests were determined by Atomic Absorption Spectrophotometry, using Shimadzu Atomic Absorption Spectrophotometer (model AA-6800, Japan) equipped with Zeaman background correction and graphite furnace at National Research Institute for Chemical Technology (NARICT), Zaria-Nigeria. The calibration curve was prepared by running different concentrations of standard solutions. The instrument was set to zero by running the respective reagent blanks.

III. Results

3.1.0 Results of the Physicochemical Analysis of the Wastewater Samples

Table 1 shows the replicate and the mean values of the physicochemical results obtained from the discharged brewery wastewater analyzed. The mean values obtained for pH and Temperature were 7.87 and 33.05°C. For Electrical conductivity, Total dissolved solutes, Dissolved oxygen, Biological oxygen demand and Chemical oxygen demand, the mean figures were as follows; 2135.00µ/cm, 495.00mg/L, 2.83mg/L, 75.75mg/L and 480.00mg/L respectively. Also, 156.50NTU, 2.55mg/L, 55.50 mg/L, 40.00 mg/L were the mean results obtained for Turbidity, Nitrate, Sulphate and phosphate respectively. These results were compared to the stipulated standards given by NESREA and WHO and the following parameters were found to be above the given limits; EC, BOD, COD, Turbidity and Phosphate, whereas pH, Temperature, Turbidity, TDS, DO, Nitrate and Sulphate where within the permissible limit.

Table 2 shows the five elements analyzed in the wastewater in order to ascertain their presence and in what concentration. They were Chromium, Nickel, Zinc, Cadmium and Lead. The following were the range of values obtained; 0.399mg/L, 0.748mg/L, 1.215 mg/L, 0.175mg/L and 1.700mg//L for chromium, nickel, zinc, cadmium, and lead respectively (Table 2). Amongst the five elements analyzed, Chromium, Nickel and Zinc were within the given limits whereas cadmium and Lead exceeded the given limits.

Table 1: Result of the Physicochemical Analysis of Brewery Wastewater

Parameter	Sample		Mean	NESREA	WHO
	A	B			
pH	7.84	7.89	7.87	6.0-9.0	6.5—8.5
Temp. (^{o}C)	36.80	29.30	33.05	<40	
EC (µs/cm)	2500.00	1770.00	2135	400	400
TDS (mg/L)	580.00	410.00	495.00	2100	1500
DO (mg/L)	3.00	2.65	2.83	7.50	7.50
BOD (mg/L)	80.10	71.40	75.75	30	<40
COD (mg/L)	520.00	440.00	480.00	250	10-20
Turbidity (NTU)	187.00	126.00	156.50	20	10
Nitrate (mg/L)	2.20	2.90	2.55	20	20
Sulphate (mg/L)	56.00	55.00	55.50	500	500
Phosphate (mg/L)	32.00	48.00	40.00	5.00	

Key**:** EC= Electrical conductivity, TDS= Total dissolved solids, BOD= Biological oxygen demand, DO= Dissolved oxygen. NTU= Nephelometric Turbidity Unit. µs/cm =Microsiemens per centimeter. mg/L= milligram per liter. NESREA= Nigerian Environmental Standards and Regulatory Enforcement Agency. WHO = World Health Organization.

Table 2: Result of the Elemental Analysis of Brewery Wastewater

Parameter	Sample		Mean	NESREA	WHO
	A	B			
Chromium (mg/L)	0.079	0.720	0.399	<0.50	<0.50
Nickel (mg/L)	0.975	0.521	0.748	<1.00	<1.00
Zinc (mg/L)	1.185	1.245	1.215	<1.00	<0.05
Cadmium (mg/L)	0.200	0.150	0.175	<0.10	<0.10
Lead (mg/L)	1.510	1.890	1.700	<0.10	<0.01

Key**:** mg/L= milligram per liter. NESREA= Nigerian Environmental Standards and Regulatory Enforcement Agency. WHO = World Health Organization.

IV. Discussion

4.1.0 pH

The mean pH value of wastewater in this study was 7.87 (table 1). Its slightly alkalinity could be accounted for due to the nature of raw materials utilized in the brewery manufacturing and cleaning processes that generates the wastewater [11]. The Nigerian Environmental Standards and Regulations Enforcement Agency's (NESREA) acceptable limit for the discharge of wastewater into surface water is between a pH of 6.0 – 9. The pH of industrial wastewater in this study was therefore within the acceptable limit. A higher mean pH value of 7.56 was previously reported for effluent from Challawa industrial area, Kano [12]. pH has been described as a measure of the amount of free hydrogen ions in water [13]. Specifically, it is the negative logarithm of the molar concentration of hydrogen ions. Because pH is measured on a logarithmic scale, an increase of one unit indicates an increase of ten times the amount of hydrogen ions. The pH of water is important because taste, corrosiveness, and the effectiveness of chlorination and coagulation in treatment processes are affected. Aquatic ecosystems also are influenced by pH. In general, pH alone is not a problem, but the combination of pH with temperature, dissolved oxygen, and the presence of various ions could pose a significant problem. Some compounds are more toxic to the aquatic organisms at different pH values. For example, the toxicity of nickel cyanide increases as the pH value decreases [13].

4.2.0 Temperature

The temperature of water or wastewater influences the chemical and biological processes and the aquatic life present in such water bodies. The amount of sunlight, rainfall, air temperature, and thermal point sources all influence the wastewater temperature. The average temperature (33.05 ^{o}C) of wastewater recorded in the study (Table 1) was found to be within the permissible limit. The maximum permissible limit set by the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for tanning, leather finishing and other industries stipulate that temperature must be less than 40 ^{0}C within 15 meters of out fall. The relatively high Temperature impacts both the chemical and biological characteristics of surface water. Increase in temperature leads to increase in solubility. At high temperatures TDS is increased as more solute goes into solution. It also affects how much oxygen the water can hold. Increased water temperature lowers the amount of dissolved oxygen available for the aquatic life present and promotes excessive growth of aquatic plants and algae. Also, the toxicity of pollutants tends to intensify with an increase in temperature [13]. Temperature is therefore important to aquatic plants and animals and the overall health of the water [14].

4.3.0 Electrical Conductivity, Turbidity and Total Dissolved Solids

The mean Electrical conductivity and Turbidity of the brewery effluents studied (2135.00µ/cm and 156.50NTU respectively) were higher than the WHO maximum permissible limit of 1000.00 µs/cm and 10.00 mg/L [15], while the mean total dissolved solid (TDS) value (495.00mg/L) was within the limit (Table1). Higher mean effluent conductivity and total dissolved solute values of 3020 µs/cm and1537.50 mg/l respectively were previously recorded for Challawa industrial area Kano [12] and a range of 1554 – 11410 µs/cm and 585.00 -7250 .00 mg/l respectively recorded for tannery in Kano metropolis [15].

Conductivity is the ability of a substance to conduct electricity. The conductivity of water or wastewater is a more-or-less linear function of the concentration of dissolved ions. Conductivity itself is not a human or aquatic health concern, but because it is easily measured, it can serve as an indicator of other water quality problems. If the conductivity of a stream suddenly increases, it indicates that there is a source of dissolved ions in the vicinity. Therefore, conductivity measurements can be used as a quick way to locate potential water quality problems. The high conductivity values recorded in this study is therefore indicative of the presence of high concentration of dissolved ions solutes and could be attributed to the large amount of chemicals used in manufacturing process [12]

Total dissolved solids (TDS) in water consist of dissolved mineral salts that change the physical and chemical properties of the water and waste water. High TDS value increases the salinity of water and thus may render it unhealthy for drinking and irrigation purposes [17]. Although fish can acclimatize slowly to higher TDS concentrations than they are accustomed, they cannot survive a sudden exposure to a high TDS concentration [16]. This makes the discharge of wastewater into surface water harmful. Consumption of water with high concentrations of TDS has been reported to cause disorders of alimentary canal, respiratory system, nervous system, coronary system besides causing miscarriage and cancer. A high concentration of TDS in water is a concern for water purveyors because it alters the taste. High TDS concentrations also exert osmotic pressure in water purification systems in hospitals and industries and exert osmotic pressure on the stream ecosystem [17].

Turbidity is a measure of the cloudiness of a liquid as a result of particulate matter being suspended within it. High turbidity is often associated with higher levels of disease causing microorganism such as bacteria and other parasites [18]. Rivers may get contaminated from soil runoff, which thereby increases its turbidity.

4.4.0 Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD)

The mean concentration of DO, BOD and COD (Table 1) of wastewater in the study fell short of the effluent discharge standard (7.5 mg/L, 30 mg/L and 250 mg/L respectively) of the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for discharge into land or surface water. DO was found to be very low between and therefore below the acceptable limits. Oxygen molecules are dissolved in water and measured as dissolved oxygen. The presence of dissolved oxygen in lakes and rivers is good because the survival of most aquatic plants depends on a sufficient level of oxygen dissolved in water. Dissolved oxygen (DO) is therefore a good indicator of healthy water quality [19].

BOD is defined as the amount of oxygen required to break down into simpler substances the decomposable organic matter present in water and wastewater at certain temperature and specified period [8]. BOD which is a very important water quality parameter that is used to evaluate organic pollution of surface water or pollution potential of effluent depends on; concentration of organic matter, extent of biological activities, temperature and other related factors. Desirable limit for BOD is 4.0 mg/L, values below 3 mg/L is required for the best use of water [7]. Discharge of effluent with a high oxygen demand directly into surface water, overloads the sensitive balance maintained in the water. Oxygen consumed in the decomposition process robs other aquatic organisms of the oxygen they need to live. Dissolved oxygen depletion in water can encourage microbial reduction of nitrates to nitrites and sulphate to sulphide giving rise to odour problems. It can also cause increase in iron II concentration [20]. A higher mean BOD value of 632.8 mg/l was reported for brewery effluents from Ibadan, Nigeria [21].

A measure of the amount of oxygen required for complete oxidation to carbon (IV) oxide and water of organic matter present in a sample of water, wastewater (effluent) called chemical oxygen demand (COD). It is another parameter used to assess the Oxygen demands of wastewater [11]. COD does not differentiate between biologically available and inert organic matter. Since nearly all organic compounds are oxidized in the COD test, COD results are always higher than BOD results; this was confirmed in this study.
Higher mean COD value of 896.3 mg/l was reported for brewery effluents from Ibadan, Nigeria [21]. Mean COD values of 91.31 ± 22.0 mg/L and 77.75 ± 10.38 mg/L respectively were reported for station I and station II at Unnao, uttar Pradesh, India for drains receiving effluents from industries[22]. Discharge of effluent with high oxygen demand into receiving surface water bodies impact it adversely.

4.5.0 Nitrate (NO_4^{2-}), Phosphate (PO_4^{3-}) and Sulphates (SO_4^{2-})

The maximum permissible limit of nitrate in drinking water is 10 mg/L [23]. The nitrate content of wastewater in this study (2.55mg/L) was lower than 10 mg/L. The amount of nitrate in water or wastewater indicates the biological contamination. Excessive concentrations of nitrate in lakes, streams and rivers greater than about 5mg/L can cause excessive growth of algae and other plants, leading to accelerated eutrophication and occasional loss of dissolved oxygen [24][25]. Nitrate concentration above drinking water quality limits can lead to blue-baby syndrome [25].

Critical levels of phosphorus in water above which eutrophication is likely to be triggered, are approximately 0.03 mg/L of dissolved phosphorus and 0.1 mg/L of total phosphorus [25]. Phosphate content of the wastewater is therefore significantly high (40.00mg/L), hence discharge into surface water may trigger eutrophication in which the growths of photosynthetic aquatic micro- and macro organisms are stimulated to nuisance levels. Excessive concentration of phosphate in drinking water may cause vomiting and diarrhea, stimulate secondary hyperthyroidism and bone loss [26].

Sulfate is associated with respiratory illness [27[. Therefore the recommended limit of sulphate content in the drinking water is 200 to 250 mg/L. The results obtained in the present study (55.50mg/L) showed that sulphate content in wastewater (Table 1) was low and discharge into flowing water may not pose serious adverse health effects. However, the average levels of sulphate in the study were higher than the natural background sulphate levels of 1.0 – 3.0 mg/l reported for unpolluted rivers in similar studies [28]. Excessive content of sulphate in water can cause laxative effect and may contribute to the corrosion of distribution systems [26].

4.6.0 Metal Concentration of the Wastewater

The results obtained in this study (Table 2) showed that three metals (Chromium 0.399mg/L, Nickel 0.748mg/L and Zinc 0.215 mg/L) out of the five analyzed were found to be within NESREA and WHO given standards whilst the remaining two (Cadmium 0.175mg/L and Lead 1.700 mg/L) exceeded the limits given. The effluent limitation standard of 0.5 mg/L for Chromium, <1.00 mg/L for Nickel and Zinc, and <0.1mg/L for cadmium and lead are the established stipulated standards by the Nigerian Environmental Standards and Regulations Enforcement Agency (NESREA) for discharge into land and surface water, zinc being the only exception. The wastewater thus constitutes serious environmental hazard. The mean effluent cadmium and chromium concentrations were found to be above both the long term trigger values (LTV) of 0.01 mg/l and 0.10 mg/l respectively set by the Australian and New Zealand Environment and Conservation Council for irrigation water [29]. The implication therefore is that wastewater from this industry is not fit for irrigation purposes and thus poses a serious risk with respect to Cadmium and chromium poisoning. The LTV value has been developed to minimize the build-up of contaminants in surface soils during the period of irrigation and to prevent the direct toxicity of contaminants in irrigation waters to standing crops. The mean zinc concentration was observed to be below the short term (5.00 mg/l) and the long term (2.00 mg/l) trigger value indicating that the use of the effluent for irrigation does not pose immediate risk with respect to zinc poisoning. Also, the use of the wastewater under study for irrigation might pose a risk with respect to lead contamination as the mean value was found to be beyond the limits under consideration although it falls within the standard for both the long term (2.00 mg/l) and short term (5.00 mg/l) trigger values of the Australian and New Zealand Environment and Conservation Council limits for irrigation water [29].Mean effluent concentration of 2.297, 1.051 and 2.986 mg/L for Chromium, lead and zinc were obtained from the effluent discharged into source of water supply in kano, Nigeria [30]. Values ranging from 0.67 mg/L to 3.10 mg/L for lead and 3.33 to 5.79 mg/L for Chromium were also reported in a tannery effluent located in Kano State [15].

Zinc is a natural component of the earth crust. Most of the zinc compounds in nature are soluble in water. The metal is essential for plants and animals but at high concentrations it becomes toxic. The Long-term trigger values and Short-term trigger values for zinc was therefore set to minimize the potential phytotoxicity of irrigation waters due to the presence of zinc. Zinc is an intestinal irritant, and the first sign of Zinc poisoning is usually intestinal distress. This includes vomiting, stomach cramps, diarrhea, and nausea. Further symptoms of Zinc poisoning are low blood pressure, urine retention, jaundice, seizures joint pain, fever, coughing, and a metallic taste in the mouth as well as induced Copper deficiency [20].

Lead is a natural constituent of the earth crust. It is the most abundant among the heavy metals with an atomic number >60. Given the evidence from solution culture of potential direct lead toxicity to plants, the Long-term trigger values and Short-term trigger values have been set in order to minimize these risks. Lead exposure in young children has been linked to learning disabilities. Lead affects both the male and female reproductive systems. In men, when blood lead levels exceed 40µg/dl, sperm count is reduced and changes occur in volume of sperm, their motility, and their morphology. A pregnant woman's elevated blood lead level can lead to miscarriage, prematurity, low birth weight, and problems with development during childhood [31]. Kidney damage occurs with exposure to high levels of lead. In acute poisoning, typical neurological signs are pain, muscle weakness, paraesthesia, and, rarely, symptoms associated with encephalitis [32].

Chromium is known in all oxidation states from -2 to +6, with +3 (chromic) and +6 (chromate) being the most common. There is no evidence that the metal is essential to plants, although traces of it are essential for humans and animals. In general, there should be few problems associated with discharges to land of wastewaters (e.g. from tanneries) containing chromium (III) because this form of chromium is reported to be relatively non-mobile [28]. Studies with nutrient solutions indicate that there may be some direct phytotoxic effect on irrigated crops of chromium in irrigation waters. Concentrations of 1–10 mg/L in nutrient solutions reduce crop yield, depending on the tolerance of different plant species and there is limited evidence that chromium (III) and chromium (VI) in nutrient solutions are about equally available to plants. It is therefore inappropriate according to Australian and New Zealand Environment and Conservation Council to set a guideline based on total chromium or chromium (III) due to the lack of evidence that chromium (III) poses a significant environmental or phytotoxic threat. Guidelines are therefore set for the chromium (VI) ion in irrigation waters based on the revised South African irrigation water quality guidelines [29].

Salts of cadmium with strong acids are readily soluble in water. Cadmium is toxic to both animals and plants at low concentration. Research also indicates that carcinogenity also may be a possibility [33]. Eating food or drinking water with high Cadmium concentration irritates the stomach causing vomiting and diarrhea. Chronic exposure can also cause irreversible damage to the lungs [34].

V. Conclusion

The results for EC (2135.00mg/L), Turbidity (156.50mg/L), BOD (75.75mg/L), COD (480.00 mg/L), Phosphates (40.00mg/L), Cadmium (0.175mg/L) and Lead (1.700mg/L) obtained from this study were found to be beyond the permissible limits stipulated by NESREA and WHO. This renders the wastewater unfit for irrigation purposes and thus calls for serious concern of the appropriate bodies. However, the level of pH, Temperature, TDS, Nitrate and sulphate were found to be within the permissible standards of NESREA and WHO.

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