PHYSICO-CHEMICAL CHARACTERISTICS OF AMA BREWERY EFFLUENT AND ITS RECEIVING AJALI RIVER IN UDI, ENUGU STATE, NIGERIA

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ABSTRACT

A study was carried out to analyse the effect of brewery effluent from Nigerian brewery Enugu on Ajali River in Eke, Udi Local Government Area, Enugu State. Brewery effluent and water samples from Ajali River were collected with sterile bottles between the month of May and June, 2013. The samples were analyzed for physicochemical properties with standard laboratory techniques. Results obtained in the study revealed that the brewery effluent had the following values: pH (7.71 ± 0.15 pH), temperature (29.50 ± 0.50^0 C), conductivity (489.00 ± 172.00 us/cm), total suspended solids (26.75 ± 0.25 mg/l), total dissolved solids (2.55 ± 0.47 mg/l), total solid (29.31 ± 0.51), biological oxygen demand (1.95 ± 0.100 mg/l), chemical oxygen demand (49.97 ± 6.00 mg/l), dissolved oxygen (3.00 ± 0.15) mg/l) and turbidity (388.00 ± 117.00 NTU). Ajali River had the following values: pH (7.69 ± 0.00 pH), temperature (26.00 ± 0.00^0 C), conductivity (280.00 ± 22.00 us/cm), total suspended solids (47.01 ± 0.99 mg/l), total dissolved solids (1.86 ± 0.24 mg/l), total solid (48.87 ± 0.11), biological oxygen demand (1.52 ± 0.12 mg/l), chemical oxygen demand (10.94 ± 2.97 mg/l), dissolved oxygen (4.37 ± 0.17 mg/l) and turbidity (278.00 ± 33.00 NTU). Objectionable water odour was recorded for both brewery effluent and Ajali River. The turbidity, total suspended solids and dissolved oxygen of both brewery effluent and Ajali River were far above the national and international permissible standard limits for effluents and surface waters. The reasons for these variations and their effect on the Ajali River were discussed.

Keywords: Physico-chemicals characteristics, Ama brewery effluent, Ajali River, Permissible limits

INTRODUCTION

Water is abundant on the planet as a whole, but fresh portable water is not always available at the right time or the right place for human or ecosystem use, it is undoubtedly the most precious natural resource vital to life (Fakayode, 2005). Rivers are open systems, which have come under increasing pressure from human activities often affecting their ecological integrity over the last century throughout the world (Ajayi and Osibanji, 1981). Industrial discharges into river are one of the causes of irreversible degradation occurring in surface water system. Due to their role in carrying industrial waste waters, rivers are among the most vulnerable water bodies to pollution. There has been significant impairment of river with pollutants, rendering the water unsuitable for beneficial purposes. Water resource of our planet is one of the most important needs for human existence and about 2.7 % of earth's water is consumable and this is threatened by pollution. Pollution as viewed by Omoleke (2004) is the environmental alteration due to man's activities detrimental to most indigenous life.

Water pollution is a major global problem which requires evaluation and revision of water resource policy at all levels (international down to individual aquifers and wells), it is suggested to be the leading cause of deaths and disease worldwide. Water pollution accounts for the death of more than 14,000 people daily (Akamiwor *et al*., 2007).

Water pollution contributes to the increased BOD by increasing the amount of organic matter present in water bodies, with organic waste containing nitrates and phosphates (additional nutrients), leading to death of plants (excess plants fight for space to grow), which will in turn affect aquatic life. Water pollution causes biomagnifications through the enhancement in the concentration of various toxic substances along the biological food chain (Ajayi and Osibanji, 1981).

Interestingly, industrial activities and urbanization in Nigeria have gradually led to the increased problem of waste disposal (Alao *et al*., 2010). Due to the role of carrying off industrial waste water; rivers are among the most vulnerable water bodies as they receive directly or indirectly these pollutants. There have been significant impairment of river with pollutants, rendering the water unsuitable for beneficial purpose such as domestic use, irrigating agricultural lands, recreation, drinking, wildlife propagating and food processing purposes in industries is on the rise, particularly in developing urban areas. Industries such as breweries that uses large amount of water for processing have the potential to pollute waterways through the discharge of their effluents into streams and rivers or by run off's and seepage of stored wastes into nearby water resources (Olorode and Fagade, 2012).

Brewery plants have been known to cause pollution by discharging effluents into receiving stream, ground water and soil (Alao *et al*., 2010). Brewery effluents comprise of waste water from washing bottles, water treatment plant, carbon dioxide generating plant, bottling and production hall and general waste water from domestic washing; they can be variable in quality and composition. The pollution discharge from brewery plants effluents come from the losses in beer production process and the clean-in-place (CIP) system located in the brewing house, cellar house and bottling house. In the examination of wastewater about 40 % of the filterable solids are organic in nature, while 75 % are suspended solids (Tchobanoglous *et al*., 1991).

The major organic matters in wastewater are protein, carbohydrates, fats and oil. They are however composed of carbon, oxygen, hydrogen, nitrogen and sulphur. Untreated brewery effluents, typically contain suspended solids in the ranges of 10 – 60 mg/l, BOD in the range of 1000 – 1500 mg/l, COD in the range of 1800 – 300 mg/l and nitrogen in the range of 30 – 100 mg/l (Alao *et al*., 2010). The most widely used analytical method of wastewater organic characteristics are the BOD, COD, total organic carbon (TOC), pH, electrical conductivity (EC) and sodium absorption ration (SAR) (Tchobanoglous *et al*., 1991). While the above parameters are measures that evaluate the interaction between the amounts of dissolved oxygen used by the living organisms in the oxidation of organic matter and the resultant effect of the carbon dioxide on water for optimum balance within the system. However, apart from the studies of Atama *et al.* (2005) on the heavy metals in effluents of two industries in southeastern Nigeria and Egwuonwu *et al.* (2012) on the evaluation of the effects of industrial wastewater discharge on surface water: A case study of Nigeria Breweries PLC, Enugu, there is need for continuous monitoring of the effects of Nigerian Breweries effluent on the receiving Ajali River.

MATERIALS AND METHODS

Sampling Sites: The samples used for this study were collected twice from Nigeria Breweries Enugu effluent discharge point and from the receiving river, Ajali River few meters away from the effluent discharge point between May and June, 2013.

Physico-chemical Study: The physicochemical parameters analysed were pH, temperature, electrical conductivity, total solids, total suspended solids, total dissolved solids, biological oxygen demand, chemical oxygen demand, dissolved oxygen, turbidity and odour using standard methods foe evaluation of water and wastewaters (Hammer, 1986; APHA, 1992; APHA, 1998; Skoog *et al.*, 1998; USEPA, 1998).

Hydrogen ion concentration (pH): The pH of the samples were measured using electronic pH meter. The pH meter was standardized by using a standard buffer solution of a known value before analyzing the samples (Skoog *et al.*, 1998).

Temperature: Temperature of the samples was recorded using the thermometric method in-situ (at the site of sampling) by the use of calibrated mercury thermometer (USEPA, 1998).

Electrical conductivity (EC): The electrical conductivity of the samples was determined using the conductivity meter (APHA, 1998).

Total suspended solids (TSS): The procedure used to obtain the suspended is as follows: a filter paper was weighed and recorder before filtering 50 mls of the samples, the filter paper was oven dried at 100^0C. TSS was calculated thus: TSS (mg/l) = (final- initial weight) x (amount of sample) – 1 x 1000 (APHA, 1992).

Total dissolved solids (TDS): The procedure is as follows: empty beaker was washed, dried and allowed to cool in a desiccator, 50 mls of the samples was measured and filtered into the weighed beaker, the sample was heated to dryness using a hot plate and the beaker was allowed to cool in a desiccator. Thereafter the beaker was weighed again. The total dissolved solid was calculated thus: weight of sample + beaker after drying – weight of empty beaker or as TDS (mg/l) = proportion of residue x 100 / volume of the sampled used (APHA, 1992).

Total solids (TS): The value was also obtained using gravimetric method. The beaker was washed and heated to dryness, allowed to cool in a desiccator and weighed. 50 mls of the sample was measured into the beaker, stirred and heated to dryness and then the beaker was allowed to cool in a desiccator and reweighed. TS (mg/l) was calculated thus: (A – B x 1000) / volume of sampled used where A = weight of beaker with residue, B = weight of beaker.

Biological oxygen demand (BOD_5): The water sample was incubated for 5 days in the dark, using the bottle incubation method (Hammer, 1986). The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biological oxygen demand. BOD = D1 – D5, where D1 = initial DO of the sample, D5 = final DO of the sample after 5 days incubation (APHA, 1998).

Chemical oxygen demand (COD): COD was determined using titration method. 10 mls of the samples was pipetted into a conical flask and 5 mls of 0.025N potassium dichromate ($K_2Cr_20_7$) was added into it, also 15 mls of concentrated tetraoxosulphate (VI) acid (H_2S0_4) was added and diluted with 40 mls of distilled water. Then 7 drops of phenoltroline ferrous sulphate indicator was added. This results into an effervescent that made the flask hot. The mixture was therefore left to cool down, during which the mixture changed to light blue green colour. The procedure was repeated for the blank (i.e. the solution without the water sample). The COD (mg/l) was calculated thus: (T_1 – T_2) x 8000 / volume of sample used, where T_1 = titre value for blank, T_2 = titre value for water sample.

Dissolved oxygen: This was observed using the Winkler's titration. 20 mls of water sample was pipetted into a conical flask. 1 ml of potassium fluoride was added into it as much as well as 2 mls of manganous sulphate 0.1N, also 2 mls of alkaline iodide acid solution and 2mls of concentrated H_2S0_4 were added into it too. Titration was with 0.025N sodium thiosulphate (NaS_20_3) until a clear solution was obtained. Then 5 mls of freshly prepared indicator was added. It was observed that the colour changed blue-black. Titration was then repeated with the sodium thiosulphate to get a colourless solution i.e. the colour of ordinary water. DO (mg/l) was calculated as: Tv x 8000 / 203.39, where Tv = titre volume of the water sample, N = normality of sodium thiosulphate used (0.025N) and

203.39 = milliliters of corrected sample and liquid.

Turbidity: Turbidity was determined using the electronic turbid meter measured in nephelometric turbidity units (NTU). Distilled water was used to calibrate the meter before pouring the samples into the AQ4500 sample chamber and covered with the vial cap, the measure key was turned on to display the values on the turbid meter.

Odour: Odour was measured using the qualitative human receptor method. Ten-man panelists were used and they were presented with questionnaire to record their feeling. The samples were collected with clean odourless bottles to half level, then covered and shaked vigorously for 3 seconds, then opened and immediately smelled by the panelist and their observations recorded. The questionnaire had options such as odour free, rotten egg, burnt sugar, soapy, fishy, septic, aromatic, chlorinous, alcoholic odour, these were further classified as objectionable or not.

Data Analysis: Means and standard error of means of the physico-chemical parameters of the different sampled effluents and river water were calculated using descriptive statistics. The one way analysis of variance (ANOVA) was used to test for any significance differences at $p < 0.05$.

RESULTS

The results of the physicochemical analyses of the Nigerian Breweries effluents and Ajali River between May and June, 2013 were presented. The values obtained for pH, temperature, electrical conductivity, total dissolved solids, total solids, biological oxygen demand, chemical oxygen demand, dissolved oxygen, turbidity and odour were clearly tabulated (Table 1).

The values obtained in the study were compared with international and national standard values for water and wastewater (WHO, 1996; NESREA, 2009), and some of the values in Nigerian Breweries effluents and Ajali River were in excess of permissible limits. Nearly all the parameters were within the permissible standards except the dissolved oxygen, total suspended solids, turbidity and odour, which does not comply with the NESREA and WHO standards.

Also electrical conductivity of the effluent was only higher than the permissible standard of WHO in the month of June. NESREA standard for electrical conductivity was not stated but the conductivity of the river was within the standard of WHO for both months. Both the brewery effluent and Ajali River gave an objectionable odour, which is unsatisfactory going by WHO and NESREA standards for odour.

DISCUSSION

Naturally, occurring freshwaters are relatively pH between 6 and 9. Most freshwaters are relatively well buffered and more or less neutral. The pH of wastewater needs to remain between 6 and 9 to protect and be beneficial to organisms (USEPA, 2004), and also 7 for drinking water (WHO, 1996). Aquatic organisms are very sensitive to the pH changes in its environment because their metabolic activities are pH dependent. In this study, the pH values obtained were slightly higher than the neutral 7 pH of water. This could be due to detergents used for washing that constituted part of the brewery wastewater. However, the values were within the permissible standards of NESREA and WHO of 6 – 9 and 6.5 – 8.5, respectively. Hence the pH of the two samples poses no threat to the aquatic organisms and the people using Ajali River for other purpose. Similar results were recorded by Otokunefor and Obiukwu (2005) while evaluating the impact of refinery effluent on the physicochemical properties of a water body in the Niger Delta, Ekhaise and Anyasi (2005) on the influence of breweries effluent discharges on the microbiological and physicochemical quality of Ikpoba River Nigeria, Alao *et al*., (2010) on the impact of brewery effluent on water quality in Majawe River, Ibadan, Southwestern Nigeria, Egwuonwu *et al.* (2012) on the effects of Nigeria Breweries PLC, Enugu industrial wastewater discharge on surface water, Olorode and Fagade (2012) on

Table 1: Physico-chemical characteristics of the brewery effluents and receiving water body (Ajali River) in the months of May and June 2013 with WHO and NESREA permissible limits

Parameter	Brewery Effluent		Ajali River		Permissible Limits	
	Mean	Range	Mean	Range	WHO	NESREA
pH	7.71 ± 0.15	7.66 - 7.76	7.69 ± 0.00	7.69 - 7.69	6.5 - 8.5	6 - 9
Temp ^{0}C	29.50 ± 0.50	30.00 - 29.0	26.00 ± 0.00	26.0 - 26.0	12 - 25	40.0
EC (us/cm)	489.00 ± 172.00	317 - 661	280.00 ± 22.00	258 - 302	400	Ns
TSS (mg/L)	26.75 ± 0.25	27.01 - 26.50	47.01 ± 0.99	46.02 - 48.00	NS	25
TDS (mg/L)	2.55 ± 0.47	2.08 - 3.02	1.86 ± 0.24	1.62 - 2.10	50	500
TS (mg/L)	29.31 ± 0.51	29.09 - 29.52	48.87 ± 0.11	47.64 - 50.10	1000	Ns
BOD (mg/L)	1.95 ± 0.100	2.08 - 1.85	1.52 ± 0.12	1.64 - 1.40	40	30
COD (mg/L)	49.97 ± 6.00	43.97 - 55.97	10.94 ± 2.97	13.92 - 7.97	80	60
DO (mg/L)	3.00 ± 0.15	3.15 - 2.85	4.37 ± 0.17	4.54 - 4.20	7.5	NS
Turbidity (NTU)	388.00 ±117.00	50.5 - 27.1	278.00 ± 33.00	311 - 245	5.0	5.0
Odour	Objectionable	Objectionable	Objectionable	Objectionable	Odourless	Odourless

Note: *Temp = temperature, EC = electrical conductivity, TSS = total suspended solids, TDS = total dissolved solids, TS = total solids, BOD = biological oxygen demand, COD = chemical oxygen demand, DO = dissolved oxygen and NS = not stated.*

the effects of brewery effluent on the physical, chemical and microbiological characteristics of its receiving stream, and Dimowo (2013) on the comparison of physicochemical parameters of River Ogun with national and international standards.

In the same vein, if temperature becomes too high or too low, the local populations of species of any biome begin to fluctuate. All the temperature values obtained in the study were within the NESREA (2009) standards for effluent discharges to surface water but did not meet the WHO guideline values (12 – 25^{0}C). In reference to WHO standard, only the brewery effluent discharge on the month of May had negative effect on Ajali River but the there was a drop in temperature value of the River, as it maintained a lower temperature of 26 ^{0}C, this could be as a result of dilution, when the effluent mixes with Ajali River. This result was in line with Alao *et al*. (2010) and Olorode and Fagade (2012) who reported 24 – 27 ^{0}C temperature range and that the temperature of the brewery effluent was within the permissible limit.

Furthermore, electrical conductivity (EC) in this study was within the WHO standards except in the brewery effluent for the month of June indicating danger and threat to aquatic organisms in Ajali River. Conductivity in brewery wastewater is largely dependent on chloride ions present in the water. Thus the higher the chloride ions, the higher the conductivity of the brewery wastewater (Nweke and Sander, 2009). Excess quantity of chloride ions can cause corrosion of iron pipes and plates. If the brewery wastewater that is high in conductivity gets into a drinking water it can introduce high amount of dissolved inorganic substances in ionized form. Thus, this effluent with high EC introduced into Ajali River may cause water imbalance problems for aquatic organisms and could decrease dissolved oxygen level. However, Ajali River after receiving a higher EC value from brewery effluent showed a decrease in EC in the month of June this could be as a result of dilution with freshwater which neutralizes the high chlorine ions content of the brewery effluent (Dimowo, 2013).

The total suspended solids of Ajali River and the brewery effluent were above NESREA permissible limits. This could be as a result of materials used for brewing like mash, spent grains, waste yeast, spent hops, grit and other inorganic substances. The values may have negative effect on the aquatic organisms found in Ajali River by decreasing light penetration, leading to a decrease in photosynthesis. The resultant primary production reduces food availability for aquatic organisms higher up in the food chain.

Suspended solids may also interfere with feeding mechanisms of filter feeding organisms such as certain benthic macro-invertebrates, the gill functioning, foraging efficiency due to visual disturbance, changes in substrate character and growth. High suspended solids in Ajali River can create anaerobic conditions and suffocate aquatic life, reducing ability to support a diversity of aquatic life (Breweries of Europe, 2002; USEPA, 2003).

Empirically, total dissolved solids concentrations are used to evaluate the quality of freshwater ecosystems. Total dissolved solids recorded in this study showed that the values are within the permissible standards of WHO and NESREA (WHO, 1996; NESREA, 2009). The result concurred with the findings of Egwuonwu *et al.* (2012) and Dimowo (2013). Furthermore, the physicochemical analysis of total solids is to ascertain dissolved solids in addition to suspended solids and settleable solids in water. The result of this study showed that the total solids of the brewery effluent and the Ajali River were within the permissible limits of WHO.

The five days biological oxygen demand (BOD_5) is the most widely used parameter in evaluating of organic pollution of surface waters. It is the amount of dissolved oxygen taken up by aerobic micro-organisms to degrade oxidizable organic matter present in streams measured over the period of 5 days. The values of biological oxygen demand of the brewery effluents and the Ajali River recorded in this study indicated that they were satisfactory and within WHO and NESREA permissible standards for effluent discharges to surface water (WHO, 1996; NESREA, 2009). This suggested that the amount of biodegradable organic matter in the brewery effluent was low and the dilution by the river water tend to reduce the dissolved oxygen demanding substances.

In relation to BOD, chemical oxygen demand is a measure of the equivalent amount of oxygen required to completely oxidize both biodegradable and non-degradable organic and inorganic matter. The chemical oxygen demand concentration at the two sampling points was within the permissible limit of WHO and NESREA standards for effluent discharges to surface water (WHO, 1996; NESREA, 2009). Similar results were recorded by Egwuonwu *et al.* (2012). Therefore, brewery effluent had no effect on COD of Ajali River.

The dissolved oxygen (DO) values were above FEPA permissible standard and WHO recommended levels of 5.0 mg/l (FEPA, 1991; WHO, 1996). This could be as result of increase in total suspended solids and turbidity from the brewery effluent, which inhibits the sunlight from reaching the submerged aquatic vegetation, thereby affecting photosynthesis. The result of this study agreed with the finding of Ikpeaiyada and Onianwa (2009), Alao *et al*. (2010) and Dimowo (2013) who reported lower values of DO in the various ecosystems studied. Decline of DO could have serious implication for the health of aquatic organism in Ajali River, because low dissolved oxygen reduces or eliminates sensitive fishes and invertebrate species. It may also lead to migration of aquatic organism. USEPA (2004) recommends that any water body that maintains aquatic life should contain 5 mg/l of dissolved oxygen for at least 16 hours of the day and the other 8 hours should not drop below 3 mg/l. Arising from the above, the brewery effluent had marked effect on the DO of Ajali River.

Importantly, the turbidity values obtained in the study at the effluent discharge and the receiving river showed higher values than the acceptable limits of WHO and NESREA (WHO, 1996; NESREA, 2009). The reason for the murky appearance of the effluent discharge is attributed to the ingredients used in brewery industries such as cereal, adjuncts, hops and yeast. All these combines with water to form wastewater which is discharged directly into the receiving river as wastewater. The murky appearance of Ajali River may also be due to the above reason in addition to other suspended solids such as clay and silt emanating from soil erosion.

Thus, the turbidity in Ajali River can inhibit light penetration needed by submerged aquatic vegetation and thus affects primary production and organisms directly or indirectly dependent on aquatic primary production. It can also affect the ability of fish gills to absorb dissolved oxygen. Moreover, Ajali River which is highly turbid and used as drinking water could increase the risk of gastrointestinal diseases in humans that use the river especially for immune compromised people who are susceptible to pathogens attached to the suspended solids. Ecologically, the level of turbidity in Ajali River can negatively influenced photosynthesis, decreased primary production and affects fish abundance. This finding was in line with the reports of Ekhaise and Anyasi (2005), Alao *et al.* (2010), Olorode and Fagade (2012) and Egwuonwu *et al*. (2012) that all reported high turbidity values in different rivers receiving brewery effluent which must have been influenced by brewery wastewater.

Finally, the odour of the brewery effluent and the Ajali river samples were objectionable. This could be as a result of dissolved organic and inorganic compound such as nitrogen, sulphur and phosphorous which emanated from putrefaction of proteins and other organic materials (Ibekwe *et al.,* 2004). Also certain gases found in brewery wastewater can cause odour. Hydrogen sulfide and ammonia gases can be toxic and pose asphyxiation hazards. The observation in this study was in line with the reports of Breweries of Europe (2002) and Egwuonwu *et al.* (2012).

Conclusion: The Ajali River in Eke, Udi local government Area of Enugu State as recipient of the brewery effluent from Nigeria Brewery (Ama Brewery) Enugu is slightly impaired and this may have negative effect on the aquatic lives. However, while brewery industries in Nigeria is an encouraging phenomenon from the economic perspective, their wastes should be effectively treated and properly managed, as the general physicochemical results showed that there were slight irregularities and inconsistencies in the effective management of their effluent discharges.

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