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Full Length Research Article

DETERMINATION OF PHYSICOCHEMICAL POLLUTANTS IN WASTEWATER AND SOME FOOD CROPS GROWN ALONG KAKURI BREWERY WASTEWATER CHANNELS, KADUNA STATE, NIGERIA

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ABSTRACT
Wastewater samples near Brewery industry and food/crop samples grown along stream were collected from the Kakuri wastewater channel near the Brewery, Kaduna metropolis. The Samples were collected between the periods of January 2017 to March 2017, to ascertain the level of the following parameters; pH, temperature, turbidity, chemical oxygen demand (COD), Biological oxygen demand (BOD_5), dissolved oxygen (DO), conductivity, total dissolved solid (TDS), sulphate, nitrate, and phosphate. Moreover, heavy metals (cobalt, chromium, iron, manganese, nickel cadmium and lead, were determined. The levels of pH, conductivity, temperature, nitrate, sulphate, phosphate, TDS, DO, BOD_5 and COD were higher than the maximum permissible limits set by Federal Environmental Protection Agencies (FEPA) Nigeria. The level of heavy metals in the wastewater and food samples were higher than limits set by the World Health Organization maximum contaminant levels and that of Food Agricultural Organisation (FAO). The high levels of heavy metals in the food samples suggests that the wastewater used for the irrigation of these food/crop samples within the study area can be tagged as polluted and is not suitable for irrigation of crops. Thus, the wastewater around the Brewery channel is highly polluted. Both Industrial and Domestic wastewater should be properly disposed and recycled.

Keywords: Brewery wastewater, Physicochemical, Pollutants, WHO and food crops

1.0. INTRODUCTION

Heavy metal ions present in food are in minute quantities; it has been established that whatever is taken as food might cause metabolic disturbance if it does not contain the permissible upper and lower limits of heavy metals (Akan et al., 2008). Thus, both deficiency and excess of essential micro-nutrients (iron, zinc and chromium) may produce undesirable effects (Konofal *et al*., 2004; Kocak *et al*., 2005). Effect of toxic metals on human health and their interactions with essential heavy metals may produce serious consequences (Abdulla and Chmielnicka, 1990). Heavy metals such as iron, lead, chromium, nickel, arsenic and cadmium are considered suitable for studying the impact of various foods on human health. Arsenic occurs naturally in food at concentration levels, which are rather essential.

Wastewater discharge from Brewery industries are major component of water pollution, contributing to oxygen demand and nutrient loading of the water bodies, promoting toxic algal blooms and leading to a destabilized aquatic ecosystem (Morrison et al, 2001; DWAF and WRC, 1995). High or low pH values in a river have been reported to affect aquatic life and alter toxicity of other pollutants in one form or the other (DWAF, 1996c). It has been established that at lower pH values in a river impair recreational uses of water and effect aquatic life. A decrease in pH values could also decrease the solubility of certain essential element such as selenium, while at the same time low pH increases the solubility of many other elements such as Al, B, Cu, Cd, Hg, Mn and Fe (DWAF, 1996c).

As a result of ammonium nitrogen in wastewater, it can lead to high nitrate concentrations. High nitrate levels in wastewater could also contribute to eutrophication effects, particularly in freshwater (OECD, 1982). Many researchers have reported to have potential health risk from nitrate in drinking water above threshold of 45 mg/l, which may give rise to a condition known as methaemoglobinemia in infants and pregnant women (Speijer, 1996; Akan et al., 2008).

Biological oxygen demand (BOD5) is the measure of the amount of oxygen requires by microorganisms for breaking down decomposable organic matter present in any water, wastewater or treated effluent to simpler substances. Alternatively, it is also taken as a measure of the concentration of organic matter present in any water. The greater the decomposable matter present, the greater the oxygen demand and the greater the BOD5 values (Ademoroti, 1996; Standard methods, 1998). Electrical conductivity of water is a useful and easy indicator of its salinity or total salt content. Wastewater effluents often contain high amounts of dissolved salts from domestic sewage. High salt concentrations in waste effluents however, can increase the salinity of the receiving water, which may result in adverse ecological effects on aquatic biota (Ademoroti, 1996).

The Kakuri Brewery site is located near Nasarawa Road in a high-density residential area of Kaduna Metropolis, Kaduna state, Nigeria. Substantial crops production takes place by the River side of the road, which are irrigated with wastewater released from the Brewery channel and serves as the main drain for built-up areas along the way. In view of the continues used of wastewater for the irrigation of crops in these area, this study is aimed to assess the levels of some physicochemical parameters in wastewater and food samples from the Kakuri Brewery.

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2.0. MATERIALS AND METHODS

2.1. Sample area and Sampling Points

Wastewater samples were collected from the Brewery channels for the analysis of physicochemical parameters. The points for the sampling were designated as Z1, Z2, Z3 and Z4. Wastewater samples were collected at the discharge point from Kakuri Brewery designated as Z1; 250 metres away from the Brewery (Z2); and at 500metres along the Kakuri stream discharged point from the Brewery and from domestic wastewater (Z3); Z4 was located at Nasarawa Bridge where substantial crops production takes place on the south east side of the road. The wastewater and food samples were sampled at these points.

2.2. Sample Collection

Wastewater samples were collected in plastic containers after cleaned by washing in non-ionic detergent, rinsed with tap water and later soaked in 10% HNO3 for 24 hours and finally rinsed with deionised water prior to usage. (Akan et al., 2008).
During sampling, sample bottles were rinsed with sampled water three times and then filled to the brim at a depth of one meter below the wastewater from each of the four designated sampling points (Z1 to Z4). The samples were labelled and transported to the laboratory, stored in the refrigerator at about 4ºC prior to analysis. Food samples such as cassava (*Manihot esculenta*), cocoyam (*Colocasia esculenta*), and tomato (*Solamum lycopersicum*) grown beside the Brewery wastewater channel down to stream, were also collected for analysis. Samples were collected between the periods of February 2017 to May 2017.

2.3. Estimation of Physicochemical pollutant indicators

All equipment and field meters were checked and calibrated according to the manufacturer's specifications. The pH meter was calibrated using HACH (1997) buffers of pH 4.0, 7.0 and 10.0. Dissolved oxygen (DO) meter was calibrated prior to measurement with the appropriate traceable calibration solution (5%HCl) in accordance with the manufacturer's instruction. The spectrophotometers (HACH DR2015) for anions determination were checked for malfunctioning by passing standard solutions of all the parameters to be measured; Blank samples (deionized water) were passed between every three measurements of wastewater samples to check for any eventual contamination or abnormal response of equipment.
The dependent variables analyzed were pH, temperature, dissolved oxygen, total dissolved solid, nitrate, sulphate, phosphate and heavy metals levels. Standard methods were followed in determining the above variables (APHA, 1998). In-situ measurements for some of the parameters, pH and temperature (°C) were measured using WTW pH Electrode SenTix 41. Dissolved oxygen was measured with Jenway Model 9070 waterproof meter. Conductivity /TDS meter (Hach model C0150) was used to measure the conductivity and total dissolved solids of the water samples. The power key and the conductivity key of the conductivity/TDS meter were switched on, and the meter was also temperature adjusted; the instrument was calibrated with 0.001M KCl to give a value of 14.7μS/m at 25ºC. The probe was dipped below the surface of the wastewater. Time was allowed for the reading to be stabilized and reading was recorded. The key was then changed to TDS key and recorded. The probe was thoroughly rinsed with distilled water after each measurement. Levels of turbidity and total suspended solid of the wastewater samples were determined using standard procedures approved by AOAC (1998).
The biological oxygen demand determination of the wastewater samples in mg/l was carried out using standard methods described by Ademoroti (1996). The dissolved oxygen content was determined before and after incubation. Sample incubation was for 5 days at 20 ºC in BOD5 bottle and BOD was calculated after the incubation periods. Determination of chemical oxygen demand was carried out using closed reflux method as described by Ademoroti (1996).

2.4. Digestion of Wastewater Samples for determination of the level of heavy Metals.

The wastewater samples were digested as follows. The sample, 100ml was transferred into a beaker and 5ml concentrated HNO_3 was added. The beaker with the content was placed on a hot plate and evaporated down to about 20ml. The beaker was cool and another 5ml concentrated HNO_3 was also added. The beaker was covered with watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO_3 was added until the solution appeared light coloured and clear. The beaker wall and watch glass were washed with distilled water and the sample was filtered to remove any insoluble materials that could clog the atomizer. The volume was adjusted to 100cm^3 with distilled water (Ademoroti, 1996). Determination of heavy metals in the wastewater samples was done using Atomic Absorption Spectrophotometer (AAS) as described in the manufacturer's instruction manual.

2.5. Digestion of food Samples for Heavy Metals Determination

The food samples were weighed to determine the fresh weight and dried in an oven at 80ºC for 72 hours to determine their dry weight. The dry samples were crushed in a mortar and the resulting powder digested by weighing 0.5g of oven-dried ground and sieve (<1mm) into an acid-washed porclain crucible and placed in a muffle furnance for four hours at 500ºC. The crucibles were removed from the furnance and cooled. 10ml of 6M HCl was added covered and heated on a steam bath for 15minute. Another 1ml of HNO_3 was added and evaporated to dryness by continuous heating for one hour to dehydrate silica and completely digest organic compounds. Finally, 5ml of 6M HCl and 10ml of water were added and the mixture was heated on a steam bath to complete dissolution. The mixture was cooled and filtered through a Whatman number 541 filter paper into a 50ml volumetric flask and made up to mark with distilled water (Akan et al., 2008).

2.6. Elemental Analysis of Digested Samples

Determination of heavy metals (cobalt, chromium, iron, manganese, nickel, cadmium, and lead) was made directly on each final solution using Perkin-Elmer Analyst 300 Atomic Absorption Spectroscopy (AAS) as described by Floyd and Hezekiah (1997).

2.7. Determination of Nitrate, Sulphate and Phosphate in the Wastewater Samples

The level of nitrate, sulphate and phosphate were determined using DR/2010 HACH Portable Data Logging Spectrophotometer.

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The spectrophotometers were checked for malfunctioning by passing standard solutions of all the parameters to be measured; blank samples (deionized water) were passed between every triplicate measurements of water samples to check for any eventual contamination or abnormal response of equipment.
Nitrate as nitrogen was determined by the cadmium reduction metal method 8036[Standard methods, 1976., DWAF, 1992]. The cadmium metal in the added reagent reduced all nitrate in the sample to nitrite; while sulphate was determined by using Sulfa Ver methods 8051 [Standard methods, 1976., DWAF, 1992].

3.0. RESULTS AND DISCUSSION

The levels of the physicochemical parameters and heavy metals are presented in Tables 1 and 2 respectively.

Table 1: The level of Physicochemical Parameters in wastewater samples from Kakuri Brewery channel, Kaduna metropolis, Kaduna State, Nigeria

Parameters	Sampling Point Z1	Sampling point Z2	Sampling pointZ3	Sampling point Z4
pH	9.92±1.30	8.92±2.04	10.32±1.42	9.56±0.52
Temp (ºC)	42.34±0.32	41.12±0.11	46.36±2.94	43.32±1.44
Turbidity (NTU)	36.34±2.13	34.24±2.32	42.24±3.10	33.36±2.01
COD (mg/l)	564.32±5.43	513.40±7.20	697.10±6.40	531.05±9.23
BOD5 (mg/l)	254.11±2.32	223.43±4.23	341.11±4.34	245.22±2.77
DO (mg/l)	7.43±0.76	6.20±0.20	8.45±0.50	6.56±0.49
TDS (mg/l)	2322.23±33.24	2212.21±22.30	2656.43±16.34	2456.20±18.80
Conductivity (μS cm^{-3})	1124.42±10.20	1022.17±12.32	1532.21±12.43	1478.32±14.32
Sulphate (mg/l)	172.30±0.83	154.20±1.02	252.31±1.32	212.22±0.78
Nitrate (mg/l)	223.21±1.21	212.43±0.32	285.33±1.64	234.56±1.92
Phosphate (mg/l)	112.45±0.42	102.23±0.10	165.20±0.56	154.22±0.67

Note: The results on Table 1 above are mean ± standard error.

The results of this study indicated that the level of pH were 9.92±1.30 and 8.92±2.04 for point Z1 and Z2 respectively, while 10.32±1.42 and 9.56±0.52 for points Z3 and Z4 respectively. Point Z3 shows the highest concentration followed by Z1, while point Z2 shows the least concentration. The mean pH values for all the sampling points were above the WHO pH tolerance limit of between 6.00 – 9.00 for wastewater to be discharged and channel into stream with exception of point Z2.

Temperature is essential for its effect on other properties of wastewater. The average temperature of wastewater under study is 42.32±0.32ºC for Z1; 41.12±0.11ºC for Z2; 46.36±2.94 ºC for Z3 and 43.32±1.44 ºC for Z4. The results indicate that some reactions might have speeded up by the discharge of this wastewater into stream. It will also reduce solubility of oxygen and amplified odour due to anaerobic reaction (less oxygen). This result is similar to research carried out by Akan et al., (2008). Moreover, these values were higher than WHO standard of 40 ºC for discharged of wastewater into stream.
Turbidity values were in the mean of 36.34±2.13NTU for Z1; 34.24±2.32NTU for Z2; 42.24±3.10NTU for Z3 and 33.36±2.01NTU for Z4. The results obtained for turbidity in the entire sampling points under investigation were higher than WHO standard of 5 NTU for discharged of wastewater into stream.
The conductivity values were 1124.42±10.20 μScm^{-3} for Z1; 1022.17±12.32 μScm^{-3} for Z2; 1532.21±12.43 μScm^{-3} for Z3 and 1478.32±14.32 μScm^{-3} for Z4. The conductivity of water is a useful indicator of its salinity or total salt content is high in the wastewater from the Kakuri stream wastewater channelled from Brewery industry. This result is not surprising, since wastewater from industrial sewage and domestic often contain high level of dissolved salts. The mean conductivity values for all the sampling point were higher than the WHO guideline values of 1000μScm^{-3} for the discharge of wastewater through channel into stream.

The mean level of Total dissolved solid (TDS) in the Kakuri Brewery wastewater channel are presented in Table 1. The concentration of TDS is 2322.23±33.24 mg/l for Z1; 2212.21±22.30 mg/l for Z2; 2656.43±16.34 mg/l for Z3 and 2456.20±18.80mg/l for Z4. The results obtained for TDS in all the sampling points were higher than WHO standard of 2000 mg/l for the discharged of wastewater into surface water. Moreover, this study resembled research carried out earlier (Akan et al., 2008).
The levels of nitrate, sulphate and phosphate in all the sampling points ranged between 212.43±0.32 to 285.33±1.64 mg/l for nitrate; 154.20±1.02 to 252.31±1.32 mg/l for sulphate and 102.23±0.10 to 165.20±0.56 mg/l for phosphate respectively. High level of nitrate, sulphate and phosphate were observed in point Z3, while low concentrations were observed for point Z2. The levels of nitrate exceeded the WHO limits of 45mg/l for nitrate in wastewater, while sulphate was below the WHO limit of 250 mg/l for the discharged of wastewater into stream. The level of phosphate in the entire sampling points were higher than the WHO limit of 5mg/l for the discharged of wastewater into river. The level of nitrate may give rise to methaemoglobinemia. The level of nitrate reported in this study in addition to phosphate level can cause eutrophication and may pose a problem for other uses.
The results obtained for Dissolved oxygen (DO) for point Z1 to Z2 varied between 6.24±0.20 to 8.45±0.50 mg/l as shown in Table 1 above. The DO is a measure of the degree of pollution by organic matter, the destruction of organic substances as well as the self-purification ability of the water body. The standard for sustaining aquatic life is stipulated at 5mg/l a concentration below this value adversely affects aquatic biological life, while concentration below 2mg/l may lead to death for most fishes (Wyasu, 2011; Chapman, 1997). The DO level at point Z1 to Z4 were above these levels.
Biological Oxygen demand (BOD5) is the measure of the oxygen required by microorganisms whilst breaking down organic matter, while Chemical Oxygen Demand (COD) is the measure of amount of oxygen required by both potassium dichromate and concentrated sulphuric acid to breakdown both organic and inorganic matters. BOD5 and COD levels of the wastewater were measured, as the two were important in unit process design (Akan et al., 2008). The wastewater has a mean COD concentration of 513.40±7.20 to 697.10±6.40 mg/l for point Z2 to Z4. BOD5 concentration of the wastewater obtained for point Z1 to Z4 ranged between 223.43±4.23 to 341.11±4.34 mg/l respectively. The concentrations of BOD and COD in all the sampling point were higher than the WHO values of 50 mg/l and 1000mg/l for the discharged of wastewater into stream. High COD and BOD concentration observed in the wastewater might be due to the use of chemicals, which are organic or inorganic that are oxygen demand in nature.

Table 2: The level of some heavy metals in wastewater samples from Kakuri Brewery channelled Kakuri stream, Kaduna metropolis, Kaduna State, Nigeria

Parameters	Sampling Point Z1	Sampling point Z2	Sampling point Z3	Sampling point Z4
Manganese (mg/l)	3.20	2.87	5.22	2.10
Cadmium(mg/l)	1.50	1.00	3.58	0.88
Lead (mg/l)	1.84	1.24	2.88	0.98
Cobalt (mg/l)	2.80	2.34	5.23	2.10
Iron (mg/l)	16.80	14.56	21.45	13.60
Chromium (mg/l)	2.20	1.56	4.33	2.00
Nickel (mg/l)	12.20	11.65	18.45	10.25

Note: The results on Table 2 above are means of each set of measurement.

The results for heavy metals concentration in wastewater samples from Kakuri Brewery wastewater channels for different sampling points were presented in Table 2. The composition of metals in the wastewater samples ranged from 2.87 to 5.22 mg/l for Mn; 1.00 to 3.58 mg/l Cd; 1.23 to 2.87 mg/l Pb; 2.34 to 5.23 mg/l Co; 14.56 to 21.45 mg/l Fe; 1.56 to 4.33 mg/l Cr; 11.65 to 18.45 mg/l Ni for point Z1 to Z4. The concentrations of heavy metals in the Brewery wastewater channels are in the following order Fe> Ni> Co> Mn> Cr> Cd> Pb. Moreover, from the results of the research study the concentrations of all the parameters are in the following order Z1>Z2<Z3>Z4. This variation is due to the fact that point Z1 is the discharged point from Kakuri Brewery, and decrease towards point Z2. The highest results obtained at point Z3 is due to the discharged of wastewater from the Domestic activities of Kaduna city area in addition to Brewery wastewater discharged into the stream which might have increase the concentration of these parameters, and finally decreases toward point Z4 due to sedimentation and dilution. This research is similar to work carried out earlier at Jakara wastewater channel in Kano metropolis (Akan et al., 2008).

Parameter	Tomatoes	Cassava	Cocoyam
Manganese (Mn) µg/g	1.24 ± 0.31	1.30 ± 0.26	1.28 ± 0.30
Cadmium (Cd) µg/g	0.32 ± 0.42	0.42 ± 0.33	0.36 ± 0.34
Lead (Pb) µg/g	0.48 ± 0.12	0.74 ± 0.22	0.50 ± 0.14
Cobalt (Co) µg/g	1.34 ± 0.54	1.86 ± 0.49	1.48 ± 0.50
Iron (Fe) µg/g	6.20 ± 0.82	7.45 ± 0.78	6.80 ± 0.81
Chromium (Cr) µg/g	0.72 ± 0.60	1.02 ± 0.50	0.92 ± 0.23
Nickel (Ni) µg/g	4.30 ± 0.30	5.42 ± 0.23	4.80 ± 0.23

Note: The results on Table 3 above are means ± standard error

The mean concentrations of heavy metal ions in food/crop samples are presented in Table 3 above. The concentrations of metals in Tomatoes are 1.24 µg/g Mn; 0.32 µg/g Cd; 0.48 µg/g Pb; 1.34 µg/g Co; 6.20 µg/g Fe; 0.72 µg/g Cr and 4.30 µg/g Ni. On the other hand, the level on heavy metal ions in Cassava are 1.30 µg/g Mn; 0.42 µg/g Cd; 0.74 µg/g Pb; 1.86 µg/g Co; 7.45 µg/g Fe; 1.02 µg/g Cr and 5.42 µg/g Ni.

Moreover, the concentration of heavy metal ions in Cocoyam are 1.28 µg/g Mn; 0.36 µg/g Cd; 0.50 µg/g Pb; 1.48 µg/g Co; 6.80 µg/g Fe; 0.92 µg/g Cr and 4.80 µg/g Ni.

From the results obtained for this study, cassava showed the highest levels of these metals, followed by cocoyam, then tomatoes exhibited the least values recorded.

The concentrations of metals in all the food/crop samples study in the present research were higher than the limits set by WHO. The high concentrations of these metals could be attributed to the used of untreated Brewery wastewater from the Brewery channel to stream by farmers for the irrigation of these crops (Audu and Lawal, 2005). The results of this study agreed with the data reported by Liu *et al*., (2005; Akan et al., 2008). In addition, results reported by some researchers (Muchuweti *et al*., 2006; Sharma *et al*., 2007) demonstrated that the plants grown on wastewater-irrigated soils are contaminated with heavy metals and pose a major health concern.

Conclusion

Based on the data collected from this research, the physicochemical parameters monitored in point Z1, Z2, Z3 and Z4 showed high levels of all the parameters. This must be as a result of the nature of wastewater from the Brewery wastewater and domestic activities in Kaduna city area. Point Z3 showed the highest concentration of the physicochemical parameter, while point Z4 showed the lowest values. The concentrations of heavy metals in all the crop/food samples were higher than values set by WHO; this high levels obtained is due to the used of untreated wastewater from the Kakuri Brewery channel for the irrigation of these food/crop samples. Accordingly, wastewater from all the sampling points are polluted as evident from the results obtained from food/crop samples.

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