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Characterization of Brewery and Pharmaceutical Industrial Wastewaters as Potential Substrates for Bioelectricity Generation

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ABSTRACT

This work evaluates the physical, chemical, and microbial characterization of brewery wastewater (BWW) and pharmaceutical wastewater (PWW) obtained from brewery and pharmaceutical industries in Nigeria for the purpose of bioelectricity generation. Characterization of the wastewater samples was performed using standard methods. The BWW and PWW physical characterization are as follows: Colour [brownish and milky-white], Odour [offensive and offensive], pH [5.4 and 5.3], Temperature [31 and 31 ^{o}C], Turbidity [7.49 and 4.0 NTU], and Total Dissolved Solid [1170 and 320 mg/l]. The chemical characterization of BWW and PWW revealed the followings; BOD [865.23l and 1346.17 mg/l], COD [438.27 and 1025.01 mg/l], Chloride [13.66 and 68.91 mg/l], Nitrate [32.843 and 11.993 mg/l], Copper [4.092 and 0.648 mg/l], Zinc [0.027 and 11.023 mg/l], and Iron [198.36 and 2.019 mg/l]. These physical and chemical parameter values were found to be much greater than the maximum permissible limits specified by WHO. This shows that the brewery and pharmaceutical industries are contributing to the local surface water pollution. The microbial characterization revealed the presence of microorganisms such as Escherichia coli, Staphylococcus species, Proteus species, Klebsiella species, and Salmonella species in both wastewaters. The presence of these microorganisms which have been implicated in organic compound degradation and heavy metal bio-accumulation indicates that both BWW and PWW can serve as potential source of substrates for bioelectricity generation through their potential ability to undergo biodegradation when subjected to biological treatment. Therefore, there is a need to develop simple, cost-effective and eco-friendly remediation systems for the treatment of BWW and PWW and simultaneous bioelectricity generation for sustainable environmental and economic development.

1. INTRODUCTION

Water is the most vital and indispensable natural resource that is required for the existence of man and all other kinds of life on this planet, but it is constantly being adversely affected both quantitatively and qualitatively by human activities (Aniyikaiye *et al.*, 2019). Presently, increasing industrialization, urbanization and developmental activities coupled with the population explosion is leading to generation of large amount of wastewater from domestic, commercial, and industrial processes (Bhatia *et al.*, 2018). Wastewater is any water that its quality has been adversely affected by anthropogenic activities (Benit and Roslin, 2015). Industrial activities generate a large number and different type of waste products and the nature of these waste depends on the industrial processes in which they originate (Surti, 2016). Industrial wastewater poses a potential hazard to natural water bodies as it contains both organic and inorganic contaminants that are toxic to various forms of life in the ecosystem (Nivruti *et al.*, 2013; Surti, 2016). The industrial wastewater contamination of these natural water bodies has emerged as a major challenge in developing and high density-populated countries like Nigeria. (Edjere *et al.*, 2016).

The brewery and pharmaceutical industries are of great economic importance to the Nigerian State due to the large growth of this sector. The brewery industry is involved in the production of fermented alcoholic beverages, such as beer and ale from cereal grains (Noorjahan and Jamuna, 2012). The brewery industry is one of the significant biggest industrial users of water that can as well cause water pollution (Kowsalya *et al.*, 2010; Enitan *et al.*, 2015). The brewery wastes are majorly composed of liquor pressed from the wet grain, solid wastes spent grains hops, still bottoms, sludges, and wash water from the various departments (Noorjahan and Jamuna, 2012). The pharmaceutical industry is engaged in the manufacture of drugs and personal care products (Dubey and Dixit, 2012). The increase in global need for keeping a healthy life has resulted in the establishment of more pharmaceutical industries in developing countries like Nigeria (Ibegbulam-Njoku *et al.*, 2013). The pharmaceutical wastewater contains a high level of pollutants such as antibiotics, animal and plant steroids, water soluble salt, reproductive hormones, vitamins in tablet forms, anti-inflammatories, analgesics, lipid regulators, anti-depressants, capsules, personal care products, glycerin, detergent metabolites, oil and grease, preservatives (such as triclosan (5-chloro-2(2,4-dichlorophenoxy)), sulfamethoxazole, and other used chemicals (i.e. spent solvents, reaction residues, used filter media, etc.) and metals (Ibegbulam-Njoku *et al.*, 2013; Babaahmadi *et al.* 2017; Kumari and Tripathi, 2019). According to Osaigbovo and Orhue (2006) about half of the global wastewater from pharmaceutical industries is released without any recommended preprocessing.

Increase in global demand for fermented beverages and drugs has made brewery and pharmaceutical industries one of the major producers of solid wastes and wastewater or effluent into the aquatic environment. When these pollutant containing wastewaters are discharged directly into the aquatic or soil environment without proper and adequate handling and treatment, they affect both the flora and fauna as well as public or human health (Olaitan *et al.*, 2014) as the toxic effects of some of these pollutants have been demonstrated (Idris *et al.*, 2013; Kumari and Tripathi, 2019). The increasing industrial pollution of water sources has prompted the need for systematic and detail characterization of industrial wastewater of various industries in Nigeria. In addition, for an effective treatment of wastewaters, a good knowledge of the quantity and quality of the waste water's composition is required.

Therefore, the main focus of this research is to determine the physical (colour, odour, pH, temperature, turbidity, electrical conductivity (EC), total dissolved solids (TDS)), chemical (chemical oxygen demand (COD)), nitrates, chlorides, metals (iron, copper, sodium, magnesium, and aluminum)) and microbial parameters (biological oxygen demand (BOD)), and microorganisms) of brewery and pharmaceutical wastewaters. The pollution parameter levels of each wastewater are compared with the standard limits as prescribed by world health organization (WHO, 2006), federal environmental protection agency (FEPA, 1991), and United State environmental protection agency (USEPA, 1999). The study presented here is part of a bigger research aiming at establishing the potential of the wastewaters to be used as substrates for bioelectricity generation when subjected to microbial fuel cell (MFC) treatment technology. MFC is a technological system in which microbial species convert the chemical energy in organic and/or inorganic compounds by sequential reactions of biodegradation or oxidation into adenosine triphosphate (ATP) in which electrons are transferred to a terminal electron acceptor to generate bioelectricity or electric current

(Chaturvedi and Verma, 2016). The impact of industrial wastewater on environmental resource loss has to be counterbalanced with resource gain that can be utilized by the society (Gemeda *et al*., 2020).

2. MATERIALS AND METHODS

2.1. Study Area

The selected two industry (brewery and pharmaceutical) for this study that generate wastewaters selected are located in Ibadan and Ilorin, respectively. The brewery industry (Nigerian Breweries Limited) is located within the geographical coordinates 7.3775° N, 3.9470° E while the pharmaceutical industry (Tuyil Pharmaceuticals Limited) is located within the geographical coordinates 8.4748° N, 4.5539° E.

2.2. Sample Collection

Wastewater samples were collected randomly from wastewater reservoirs of the two industries into two (2) separate clean 25 L plastic containers (with air-tight covers) that had been previously rinsed with the respective wastewaters prior to collection**.** Each wastewater sample collected was left undisturbed for 24 hours at room temperature (25 ^oC).

2.3. Chemicals, Reagents, and Glassware

The chemicals and reagents used for this study were of analytical grade (BDH chemicals, UK). The glassware used in the course of study was of "A" grade calibrated quality.

2.4. Physical, Chemical, and Microbial Characterization

The wastewater samples (Brewery wastewater (BWW) and Pharmaceutical wastewater (PWW) were analyzed for pH, temperature, total dissolved solids (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD), nitrates, chlorides, and metals (iron, zinc, copper, sodium, magnesium, and aluminium). The methods used for the wastewater analyses were according to the standard procedures described for the examination of water and wastewater by American Public Health Association (APHA, 2005). The colour, odour, pH, temperature, dissolved oxygen (DO), turbidity, and electrical conductivity (EC) of the wastewater samples were analysed at the point of collection (i.e., on-site) before their onward transportation to the laboratory. The pH was measured using a portable digital analysis meter (HQ40d, HACH, USA). EC was measured with the use of a portable HACH conductivity metre. Temperature and DO were measured by a portable DO meter (HI 9143, HANNA, Italy) (DO-200, Lovibond, Germany). Turbidity was measured using a Turbicheck Turbidity meter (The Tintometer Limited, Lovibond House, Amesbury, UK).

2.4.1. Total dissolved solids

TDS in the wastewater sample was quantified by gravimetric method. A clean petri-dish was oven-heated to a temperature of 100 ^oC and thereafter cooled in a desiccator and then weighed to constant weight. Using a pre-weighed filter paper, the collected wastewater sample was filtered into a clean conical flask. A known volume of the filtrate was poured into the petri-dish and oven-heated at temperature of 180 ^oC. The obtained residue was then cooled in the desiccator and weighed to a constant weight. The TDS is calculated with Equation 1.

$$TDS\,(mg/l) = \frac{(W_1 - W_2)\times 1000}{Volume\ of\ Wastewater\ (ml)} \tag{1}$$

Where W_1 = weight of Petri dish + dried residue (mg) and W_2 = weight of Petri dish (mg)

2.4.2. Biological oxygen demand

The BOD of the collected wastewater samples was determined using the dilution method. Dilution water was prepared by adding 10 ml each of the following reagents; phosphate buffer, ammonium chloride (NH_4Cl), calcium chloride ($CaCl_2$), ferric chloride (FeCl), magnesium sulphate ($MgSO_4$), and sodium sulphite ($NaSO_3$) into 10 L of distilled water. A measured volume of the wastewater sample in a 1 L standard flask was topped up with dilution water to 1 L mark of the flask. Two 300 mL amber bottle were completely filled with the diluted water. One of the bottles was incubated at 20 ^oC for 5 days while into the other amber bottle was added manganese sulphate ($MnSO_4$) solution, alkali-iodide-azide reagent, and concentrated sulphuric acid (H_2SO_4). Dissolved oxygen (DO) in the wastewater sample was derived through iodometric titration. For DO at day zero (DO_0), 50 ml aliquot of the solution was titrated against sodium thiosulphate solution using starch solution as indicator, until a colourless end-point was attained. At the end of the 5 days incubation, the sample in the incubator was brought out, DO at day five after incubation (DO_5) was determined using the same procedure that was used for the DO_0 determination. A blank was prepared in a transparent bottle for DO_0 while another blank was prepared in an amber bottle and incubated with the sample for DO_5. The BOD was calculated using Equation 2.

$$BOD(mg/l) = \frac{(DO_0 - DO_5) \times Volume\ of\ BOD\ Bottle}{Volume\ of\ Wastewater(ml)} \quad (2)$$

2.4.3. Chemical oxygen demand

COD determination in water basically involves the water sample reaction with strong oxidising agent which oxidizes the organic matter in it. The wastewater COD was obtained using the open reflux method. This was conducted by the addition of mercuric sulphate ($HgSO_4$) and H_2SO_4 into an aliquot of wastewater sample in a reflux flask. After cooling, the obtained solution was reacted with known concentration of potassium dichromate ($K_2Cr_2O_7$) and known volume of H_2SO_4. The solution was refluxed for 2 h and then cooled. The cooled solution was thereafter diluted to twice its volume and further cooled to room temperature. The excess $K_2Cr_2O_7$ present in it was determined by titrating the cooled solution with ferrous ammonium sulphate ($FeNH_4SO_4$) using ferroin indicator. Similarly, a blank with all reagents added to 25 ml of distilled water was also titrated. Equation 3 was utilized to estimate the COD.

$$COD(mg/l) = \frac{(V_1 - V_2) \times N \times 8000}{Volume\ of\ Wastewater(ml)} \quad (3)$$

Where V_1 = titrant volume used for the sample (ml); V_2 = titrant volume used for the blank (ml); and N = normality of the $FeNH_4SO_4$.

2.4.4. Nitrates

The UV spectrometric method was used in the determination of nitrate (NO_{3-}) in wastewater. A 100 mg/l standard stock solution of nitrate was prepared by dissolving 0.72 g of anhydrous potassium nitrate (KNO_3) in 1 L of distilled water. Serial dilutions from the nitrate stock solution were done for the preparation of calibration standards for nitrate in the range 0.1–1.0 mg/l. A series of reaction tubes was set up in test tube stand and placed in a cold-water bath. Measured volume of wastewater sample was poured into the reaction tubes while sodium chloride (NaCl) solution and H_2SO_4 was each added sequentially. Thereafter, Brucine-sulphanilic acid reagent was added and the mixture was then heated for some minutes in a boiling water bath. The samples were then allowed to cool and the absorbance of each sample was measured at 410 nm in the UV spectrometer in comparison with the reagent blank. The nitrate- nitrogen ($NO^{3-}N$) concentration was then estimated from the calibration curve by extrapolation.

2.4.5. Chlorides

The Mohr's method (Shukla and Arya, 2018) was adopted in the determination of chloride (Cl^-) ions concentration in the wastewater. A known volume of wastewater sample was titrated against a known concentration of standard silver nitrate solution using chromate ion as indicator. After all the chloride has been precipitated as white silver chloride, the first excess of titrant resulted in the formation of a brownish red silver chromate precipitate, indicating the end point.

2.4.6. Determination of total metals

The wastewater samples were digested using nitric acid as the digester or oxidising agent and the digest were analyzed using Atomic Absorption Spectrophotometry (AAS, Perkin—Elmer, Melville, NY, USA). Calibration curves were plotted for each of the metals separately, by running various concentrations of standard solutions at specified wavelengths. A reagent blank sample was also analysed. The metal concentration was obtained from the difference between the sample readings and the blank readings.

2.4.7. Microbial enumeration, isolation, and identification

The isolation and enumeration of bacteria in BWW and PWW was carried out in line with the serial dilution and pour or spread plate technique (APHA, 2005) using Oxoid agar as nutrient (i.e., nutrient agar (NA)). The wastewater was filtered and 0.1 ml aliquots of the wastewater was serially diluted from $10^{-1} – 10^{-3}$ which were then poured and spread on NA plates that contained droplets of crude oil. Nystatin was added to prevent fungal growth and the NA plates were then incubated at 37 °C for 18-24 hours. After incubation, plates that yielded 30-300 growth of bacterial colonies were isolated and accepted. The pure isolated bacterial species were identified and characterized based on Bergey's manual (Krieg *et al*., 1994; Saroj and Keerti, 2013).

3. RESULTS AND DISCUSSION

3.1. Physical Characterization

Results of the physical characterization are given in Table 1.

3.1.1. Colour and odour

Colour of wastewaters typically depends on different industrial processes that must be assessed on a case-by-case basis (Benit and Roslin, 2015). It is used to assess the condition of wastewater with respect to how long it has been in a sewer. Table 1 shows that the BWW has a milky-white colour with colour rating of 4.60 TCU as well as an offensive and objectionable odour. This observed colour is different from the brownish black colour observed by Noorjahan and Jamuna (2012) and Kowsalya *et al.* (2010) for the BWW gotten from one of the industries in India. These workers also reported similar observation of an offensive odour for the brewery wastewater. The PWW presented a brownish colour with colour rating of 8.04 TCU as well as possessing an offensive pungent objectionable odour. The brownish colour observed for PWW in this study is quite different from the purple colour, yellow colour, and colourless colour that was respectively observed by Olaitan *et al.* (2014) for three set of PWW obtained from Sango Area of Ogun State, Nigeria. Olaitan *et al.* (2014) have also reported a similar observation of an objectionable odour for the three set of PWW. The observed colour and odour of these wastewaters could be attributed to the organic and inorganic matter decomposition in the wastewaters (Noorjahan and Jamuna, 2012).

Table 1: Results of the physical characterization of BWW and PWW

Parameter	BWW	PWW	FEPA[a]	USEPA[b]	WHO[c]
Colour (TCU)	4.60 (milky-white)	8.04 (brownish)	NS	NS	NS
Odour	Offensive	Offensive	NS	NS	NS
Temperature (ºC)	31.0	31.0	NS	NS	20-35 ºC
pH	5.3	5.4	6.0-9.0	6.5-8.5	6.0-9.5
Turbidity (NTU)	4.0	7.49	NS	NS	5.0
Electrical Conductivity (µS/cm)	2340	640	NS	NS	NS
TDS (mg/l)	320	1170	2000	500	< 1200

*Values are means of 3 replicates. NS: Not stated; [a]Federal Environmental Protection Agency (1991) permissible limits for effluents discharged into surface water; [b]United States Environmental Protection Agency (1999) national recommended water quality criteria-correction; [c]World Health Organization (2006) guidelines for drinking water recommendation

3.1.2. pH and temperature

pH is a measure of acidity or alkalinity and is one of the stable parameters that specify a relative amount of free hydrogen and hydroxyl ions in the water. It is a simple parameter but extremely important, since most of the chemical reactions in aquatic environment are controlled by any change in its value (Ram, 2011). Aquatic organisms are sensitive to pH changes. Also, biological treatment requires pH control monitoring. The pH of BWW sample was obtained to be 5.3 while that of PWW was 5.4 (Table 1). These values indicated that the wastewaters are relatively acidic (Wakuma and Fita, 2017). In both cases, pH values were below the permissible limits of 6.0-9.0, 6.5-8.5, and 6.0-9.5 specified by FEPA, USEPA, and WHO, respectively. Kowsalya et al. (2010) have similarly reported an acidic pH for BWW while Noorjahan and Jamuna (2012) and Gemeda *et al.* (2020) have respectively reported an alkaline pH for BWW obtained in India and Sabata of Ethiopia, respectively. Also, the acidic pH observed for PWW is in agreement with the observation reported by Oliveira Júnior *et al.* (2013), Olaitan et al. (2014), and Kumari and Tripathi (2019) for PWW obtained in Anápolis, Goiás of Brazil, Sango Industrial layout of Nigeria, and Uttar Pradesh of India, respectively. Nevertheless, the pH values of the BWW and PWW were within the allowable range between 4.0 and 9.5, which is suitable for most bacteria survival (Agarry *et al.*, 2020). Most bacteria cannot survive outside this pH range (Shao et al., 2014; Agarry *et al.*, 2020). The pH results thus suggest that the BWW and PWW was conducive or suitable to be used as a substrate for bioelectricity generation.

Temperature is one of the most important ecological features that controls behavioural characteristics of organisms, solubility of gases and salts in water. The temperature of wastewater is important primarily because it affect the aquatic and biological life in receiving water bodies. Change in temperature affects the wastewater in a number of ways; firstly, as the temperature rises, its viscosity increases with a corresponding increase in its tendency to precipitate. Extremely low temperature adversely affects the efficiency of sedimentation. Secondly, the bacterial activity increases with increase in temperature up to about 60 °C. Thirdly, the solubility of gases in wastewater decreases with increase in temperature (Abdel *et al.,* 2010). Higher temperatures tend to lower the dissolved oxygen solubility which is detrimental to the living organisms in the water. The temperature of BWW and PWW was each measured to be 31 ºC (Table 1). The values are comparable to the standard permissible limit provided by both WHO and FEPA. The temperature results for BWW and PWW in Table 1 suggest that it favours both mesophilic microbial growth and organic matter biodegradation and thus BWW and PWW could be utilized as a substrate for bioelectricity generation. This is because high wastewater temperature, with an optimum temperature range of 30–40 °C, significantly induce the activity of microorganisms and biodegradation. However, if the temperature falls below 20 °C, the rate of microbial activity and biodegradation is found to be slower.

3.1.3. Turbidity and electrical conductivity

Turbidity which is a measure of suspended materials in the water was found to be relatively low for BWW (4.0 NTU) and PWW (7.49 NTU), respectively (Table 1). The turbidity of a wastewater depends on the strength of the wastewater, the stronger the concentration of the wastewater the higher its turbidity (Sawyer, 1994). The turbidity concentration values obtained for BWW and PWW were found to be relatively lower than the values of 88.6 NTU reported by Edjere *et al.* (2016) for BWW and range of 40-120 NTU obtained by Olaitan *et al.* (2014) for three set of PWW. Electrical conductivity (EC) is a measure of the sample's ability to conduct current (Aniyikaiye *et al.*, 2019). This is attributed to dissolved organic and inorganic ions in the wastewater (Agoro *et al.*, 2018). Inorganic ions have the most significant influence on the water conductivity. High values of EC implies that inorganic ions are abundantly present in the wastewater. Hence, EC is directly proportional to the TDS concentration. That is, high EC in wastewater is an indication of high TDS concentration. Therefore, it implies that the ability of an electric current to pass through the wastewater is proportional to the ionic solutes' concentration dissolved in the water (Aniyikaiye *et al.*, 2019). The EC values for BWW and PWW were found to be 2340 (µS/cm) and 640 (µS/cm) (Table 1), respectively. The EC value for BWW is relatively higher than that of PWW which indicates the presence of more inorganic ions in BWW than PWW. The EC value obtained for BWW in this study is relatively higher than the EC values of 829 µS/cm and 1320 µS/cm reported by Edjere *et al.* (2016) and Gemeda *et al.* (2020) but lower than the EC values of 3585 µS/cm and 3695 µS/cm reported by Noorjahan and Jamuna (2012) and Kowsalya *et al.* (2010) for BWW obtained in Tamil Nadu (India) and Tamil Nadu (India), respectively. Similarly, the EC value obtained for PWW in this study is relatively higher than the EC values of 199-413 µS/cm reported by Olaitan *et al.* (2014) for PWW obtained in Sango Industrial Layout (Nigeria) but lower than the EC values of 1563.34 µS/cm reported by Kumari and Tripathi (2019) for PWW obtained in Uttar Pradesh (India). The relatively high EC values obtained for BWW and PWW in this study indicates that both wastewaters possess the potential to be utilized as substrates for bioelectricity.

3.1.4. Total dissolved solids

TDS being a measure of all dissolved substances in water was found to be 1170 mg/l for BWW and 320 mg/l for PWW (Table 1). These values are relatively lower than the maximum permissible limit of 2000 mg/l and < 1200 mg/l specified for wastewaters by FEPA and WHO, respectively. TDSs are majorly composed of inorganic salts (bicarbonates, chlorides, carbonates, phosphates, and nitrates of calcium, magnesium, sodium, and potassium; manganese; salt), organic matter, and other dissolved particles (Benit and Roslin, 2015; Aniyikaiye *et al.*, 2019). By implication, TDS is also a measure of salinity. A high content of dissolved salts affects density of water, influences the osmoregulation of fresh water in organisms, and reduces solubility of gases. In comparison with other similar wastewater, the TDS value obtained for BWW in this study is relatively higher than the TDS values of 552.97 mg/l and 1320 µS/cm reported by Edjere *et al.* (2016) for BWW obtained in Benin (Nigeria) but lower than the TDS values of 1400 mg/l, 2712 mg/l and 2100 mg/l reported by Myina *et al.* (2014), Noorjahan and Jamuna (2012), and Kowsalya *et al.* (2010) for BWW obtained in Jos (Nigeria), Tamil Nadu (India), and Tamil Nadu (India), respectively. Similarly, the TDS value obtained for PWW in this study is relatively higher than the TDS values of 134-277 mg/l reported by Olaitan *et al.* (2014) for PWW obtained in Sango Industrial Layout (Nigeria) but lower than the EC values of 1563.34 µS/cm reported by Kumari and Tripathi (2019) for PWW obtained in Uttar Pradesh (India).

3.2. Chemical Characterization

Results of the chemical characterization are provided in Table 2.

3.2.1. Biochemical and chemical oxygen demand

The required oxygen demand expressed as BOD and COD is an important parameter for the evaluation of wastewater organic pollutant load (Speer, 1995). The COD is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. BOD is a measure of the oxygen amount in water utilised by microbial species to decompose organic matter (Aniyikaiye *et al*., 2019). BOD and COD tests are used to determine the pollution extent of a wastewater and the efficacy of effluent or wastewater treatment methods. The BOD and COD values are measure of the relative oxygen-depletion effect of a waste contaminant. The higher the BOD value or concentration, the greater the extent of oxygen depletion in the water bodies. This leads to reduction in the oxygen available for microorganisms and other forms of higher aquatic life which consequently results in their death (Rachna and Disha, 2016; Aniyikaiye *et al*., 2019). Table 2 shows that the BOD values for BWW and PWW were 865.23 mg/l and 1346.17 mg/l, respectively. These values are higher than the 50 mg/l maximum permissible limits specified by FEPA and WHO. The high BOD values for BWW and PWW indicates high availability of organic compounds (or matter) in the wastewaters. Discharge of wastewater with high BOD level into aquatic bodies can lead to serious dissolved oxygen depletion and death of aquatic life in the receiving water bodies. To compare the BOD values obtained in this study with other similar wastewater, it is observed that the BOD value obtained for BWW in this study is relatively higher than the BOD values of 2.85 mg/l, 209 mg/l, 260 mg/l, 230 mg/l, 14.38 mg/l reported by Edjere *et al.* (2016), Gemeda *et al.* (2020), Noorjahan and Jamuna (2012), Kowsalya *et al.* (2010), and Myina *et al.* (2014) for BWW obtained in Benin (Nigeria), Sabata (Ethiopia), Tamil Nadu (India), Tamil Nadu (India), and Jos (Nigeria), respectively. Similarly, the BOD value obtained for PWW in this study is relatively higher than the BOD values of 22-60 mg/l reported by Olaitan *et al.* (2014) for PWW obtained in Sango Industrial Layout (Nigeria) but lower than the BOD values of 7253.34 mg/l and 1720 mg/l reported by Kumari and Tripathi (2019) and Ibegbulam-Njoku *et al.* (2013) for PWW obtained in Uttar Pradesh (India) and Aba (Nigeria), respectively.

Table 2: Results of the chemical characterization of BWW and PWW

Parameter	BWW	PWW	FEPA[a]	USEPA[b]	WHO[c]
BOD (mg/l)	865.23	1346.17	50	NS	50
COD (mg/l)	438.27	1025.01	NS	NS	100
Chloride (mg/l)	13.661	68.911	600	250	250
Nitrate (mg/l)	32.843	11.993	20	10	50
Copper (mg/l)	4.092	0.648	<1	0.009	NS
Zinc (mg/l)	0.027	11.023	<1	0.12	0.01
Iron (mg/l)	198.36	2.019	20	0.3	-

The COD values for BWW and PWW are 438.27 mg/l and 1025.01 mg/l, respectively (Table 2). It was observed that the COD values are very much higher than 100 mg/l which is the maximum permissible limit specified by WHO. The BOD values of BWW and PWW are relatively higher than their corresponding COD values. The BOD/COD ratio of wastewater is referred to as the biodegradability index which is a parameter prior to treatment tentatively indicates the biodegradability of the wastewater (Aniyikaiye *et al*., 2019; Agarry *et al*., 2020). Wastewater with BOD/COD value greater than 0.6 or COD/BOD value greater than 1.14 is considered fairly or easily biodegradable and could therefore be effectively treated biologically (Aniyikaiye *et al*., 2019; Agarry *et al*., 2020). The high BOD/COD values of 1.97 and 1.31 obtained for BWW and PWW indicates the presence of high level of easily biodegradable compounds and thus the wastewaters can easily and effectively be treated by biological method and be used as substrates for bioelectricity generation. However, for the sustainability of aquatic life, it is essential for the water bodies to have reduced level of BOD/COD values (Aniyikaiye *et al*., 2019). Comparison of the COD values obtained in this study with other similar wastewater, it is observed that the COD value obtained for BWW in this study is relatively higher than the COD values of 5.69 mg/l and 210.5 mg/l, reported by Edjere *et al.* (2016) and Gemeda *et al.* (2020) however, lower than the COD values of 854 mg/l, 643 mg/l, and 8308.66 mg/l reported by Noorjahan and Jamuna (2012), Kowsalya *et al.* (2010), and Myina *et al.* (2014) for BWW obtained in Benin (Nigeria), Sabata (Ethiopia), Tamil Nadu (India), Tamil Nadu (India), and Jos (Nigeria), respectively. Similarly, the COD value obtained for PWW in this study is relatively higher than the COD values of 80-110 mg/l and 756.67 mg/l reported by Olaitan *et al.* (2014) for PWW obtained in Sango Industrial Layout (Nigeria), and Kumari and Tripathi (2019) for PWW obtained in Uttar Pradesh (India) but lower than the COD values of 5680 mg/l reported by Ibegbulam-Njoku *et al.* (2013) for PWW obtained in Aba (Nigeria).

3.2.2. Chloride and nitrate

For safety purposes, the concentration of chloride in wastewater should not exceed 250 mg/l as specified by USEPA and WHO, respectively. However, according to the results in Table 2, the chloride concentration presents in the BWW and PWW are 13.661 mg/l and 68.911 mg/l, respectively which are exceedingly lower than the FEPA, USEPA, and WHO maximum permissible limit. This low value may be as a result of low concentration of chlorides in raw materials used for various processes (Kolhe *et al.*, 2008). In aquatic bodies, high levels of chloride can be a threat to the ecological food sources sustainability, thereby posing a risk to the survival of microbial species, growth, and reproduction (Imo *et al.*, 2017). These very low values of chloride concentration in BWW and PWW makes the wastewaters suitable as substrates for bioelectricity generation as it will not serve to inhibit microbial activity in the course of organic matter biodegradation. Nitrate is important in water pollution because it serves as an effective limiting nutrient source for algae in aquatic systems (Rachna and Disha, 2016) and as indices for eutrophication in water bodies (Edjere *et al.*, 2016). Nitrates are the end product of the aerobic decomposition of organic nitrogenous matter (organic nitrogen is converted to ammonia and then ammonia is oxidized to nitrate) (Walakira and Okot-Okumu, 2011; Rachna and Disha, 2016). The values of nitrate in both samples of BWW and PWW were 32.843 mg/l and 11.993 mg/l, respectively (Table 2). The nitrate concentration present in BWW is below the maximum permissible limit of 50 mg/l, however, higher than the values of 20 mg/l and 10 mg/l specified by FEPA and USEPA, respectively. While the nitrate concentration in PWW is lower than the values of 20 mg/l and 50 mg/l respectively specified by FEPA and WHO but slightly higher than the value of 10 mg/l specified by USEPA. Excessive presence of nitrate in conjunction with phosphate and potassium causes algal blooms which can result in the death of aquatic organisms (Rachna and Disha, 2016). The nitrate concentration obtained for BWW in this study is relatively higher than the nitrate concentrations of 14.60 mg/l reported for BWW obtained from Benin (Nigeria) by Edjere *et al.* (2016) while the chloride concentration is lower than the value of 90.96 mg/l, 22.87 mg/l, and 804 mg/l reported for BWW obtained from Benin (Nigeria), Jos (Nigeria), and (India) by Edjere *et al.* (2016), Myina *et al.* (2014), and Noorjahan and Jamuna (2012), respectively. Also, the obtained nitrate and chloride concentrations for PWW is observed to be higher than the nitrate concentration of 1.52-331 mg/l and chloride concentration of 10-18 mg/l reported by Olaitan *et al.* (2014) for PWW gotten from Sango (Nigeria). The presence of nitrate in both BWW and PWW other than oxygen could serve as terminal electron acceptor in microbial fuel cell (Chaturvedi and Verma, 2016) and thus confer on the wastewaters the potential for it to be used as substrates for bioelectricity generation.

3.2.3. Metals

Heavy metals are non-biodegradable and are found to be potentially toxic even at low concentrations (Malakootian *et al.*, 2009; Adekunle *et al.*, 2012). Nonetheless, some of these metals like copper, zinc, and iron play integral and essential role as micronutrients in microbial metabolic processes, however, can be toxic at higher concentrations by inhibiting various cellular or biochemical processes through forming unspecific complex compounds within the microbial cell (Agarry *et al.*, 2019). While many other metals such as cadmium, lead, silver and mercury are not essential and thus do not possess any biological role (Agarry *et al.*, 2019). Micro-elements such as copper, zinc, and iron were found to be present in both BWW and PWW samples. The values of copper, zinc, and iron in BWW are 4.092, 0.027, and 198.36 mg/l, respectively. The copper and iron concentrations are higher than the maximum permissible limit while zinc concentration is lower than the permissible limit directed by FEPA and USEPA. The values of copper, zinc, and iron in PWW are 0.648, 11.023, and 2.019 mg/l, respectively. Also, the concentrations of copper and zinc in PWW are higher than the maximum permissible limits specified by FEPA and USEPA while the iron concentration is below the maximum permissible given by FEPA but higher than that given by USEPA. The concentrations of copper and iron present in BWW were found to be relatively higher than the concentrations (copper, 0.31 mg/l: iron, 8.10 mg/l; copper, 0.30 mg/l: iron, 3.27 mg/l) and zinc concentration lower than the concentrations of 0.58 mg/l and 0.21 mg/l reported by Edjere *et al.* (2016) and Myina *et al.* (2014) for BWW. Also, the copper and iron concentrations in PWW were observed to be relatively higher than the concentrations (copper, 0.15-0.28 mg/l: iron, 0.20-0.34 mg/l) and zinc concentration within the range of 1.75-2.62 mg/l reported by Olaitan *et al.* (2014) for PWW. The sodium present in both samples were 22.193 and 71.032. This shows that the sodium in brewery wastewater was within the limits while that of pharmaceutical wastewater exceeds the limit specified by WHO (2006).

3.2.4. Microbial characterization of wastewater samples

The result of microbial characterization which included the total microbial counts and the characterized isolates from the wastewaters (PWW and BWW) are presented in Table 3.

Table 3: Microbial characterization of brewery and pharmaceutical wastewater

Type of wastewater	Organisms isolated	Total count (x 10^2) cfu/ml
BWW	*Pseudomonas aeruginosa; Staphylococcus aureus; Escherichia coli; Streptococcus faecalis; Klebsiella aerogenes; Salmonella shegella; Proteus mirabilis*	34.6
PWW	*Staphylococcus aureus; Escherichia coli; Klebsiella pneunoniae; Salmonella shegella; Proteus mirabilis; Cndida albican; Proteus vulgularis; Klebsiella spp*	83.9

Seven (7) and eight (8) strains of bacteria were isolated and identified in BWW and PWW, respectively. *Staphylococcus aureus, Esherichia coli, Salmonella shegella; Proteus mirabilis* and *Klebsiella spp* are found in both wastewater samples while *Pseudomonas aeruginosa* was found in BWW and *Candida albican* was found in PWW. Most of these microbial species (*Pseudomonas aeruginosa*, *Staphylococcus aureus, Escherichia coli*, *Proteus vulgaris* and *Klebsiella pneumonia*) have been implicated in their potential to biodegrade organic compounds and bioaccumulate heavy metals (Obahiagbon and Owabor, 2008; Oaikhena *et al*., 2016; Obayori *et al*., 2017; Ozyurek and Bilkay, 2018; Agarry *et al*., 2019). Therefore, this observation indicates that both wastewaters (BWW and PWW) can serve as substrates for bioelectricity generation.

4. CONCLUSION

Wastewaters from two different industries; brewery and pharmaceutical, were collected and analysed for their physical, chemical, and microbiological parameters as to determine their impact on water pollution and evaluate their potential or suitability as substrates for bioelectricity generation. The wastewater quality parameters like BOD, COD, and TDS were found to be significantly higher than the maximum permissible limit respectively prescribed by FEPA, USEPA, and WHO. This clearly shows that the brewery and pharmaceutical industries in Ibadan and Ilorin (Nigeria) are polluting the local surface water bodies. However, values of the physical, chemical, and microbial parameters and the presence of potential organic compound degraders and heavy metal bio-accumulators in the wastewaters revealed that the brewery and pharmaceutical wastewaters can serve as potential source of substrates for bioelectricity generation through their potential ability to undergo biodegradation when subjected to biological treatment. Therefore, there is a need to develop simple, cost-effective and eco-friendly remediation systems for the treatment of brewery and pharmaceutical wastewaters and simultaneous bioelectricity generation to minimize water pollution for sustainable environmental and economic development.

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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