Characterization of brewery waste water and evaluation of its potential for biogas production

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Abstract: The issue of global warming and climate change is strongly receiving public attention and has become a major environmental concern both nationally and internationally. Brewing industries are among the largest consumers of water and the largest source of organic effluent mostly from the brewing, cleaning, and cooling processes which must be treated to allowable levels to reduce environmental pollution. Close to 10 L water is used for every 1 L beer that is brewed, though the amount of water in the final beer is small. A study was undertaken to characterize and assess the variations in the quality of untreated brewery waste water. Samples from different process streams including brewing line, clean in place line and mixing line from two brewing industries in Kenya were analyzed for BOD5, COD, TDS, TSS, sodium, total nitrogen and phosphorous using standard method as per American Public Health Association (APHA). There was a significant variation ($p<0.001$) in the all the physicochemical parameters between the industries and a significant interaction ($p<0.001$) between sampling point and the company. Analysis of the BOD to COD ratio showed the biodegradability index to range from 0.039 to 0.567 for brewing line, 0.177 to 0.766 for cleaning in place and 0.776 to 0.911 for mixing point, thus the waste water was found to be easily biodegradable at the mixing point for all the industries. However pretreatment would be required to improve anaerobic digestion.

Keywords: brewery, physicochemical characterization, waste water, pollution, biodegradable, anaerobic digestion

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1 Introduction

Brewery is one of the traditional industries with an important economic value in the agro-food sector. Processing of beer involves both chemical and biochemical reactions which include mashing, boiling, fermentation and maturation. Other processes are wort separation, wort clarification, rough beer clarification and filtration. For every 1,000 t of beer produced, 137 t to 173 t of solid waste may be created in the form of spent grain, trub from wort production and waste yeast (Caliskan et. al., 2014). Water usage in brewing industries varies widely among breweries and is dependent upon specific processes and location. The main water using areas within the brewery include brew house, cellars, packaging and utilities such as boiler house, cooling and amenities. Water use attributed to these areas includes the water used in the product, rinsing and cleaning of process equipment, flushing of filters, keg washing, cleaning of packaging materials, general washing and soap lubrication of conveyors in packaging area, which are of considerable importance, in terms of composition of the effluent that end up to waste stream (Zheng et al., 2015). In addition, the quantity and quality of the effluent can vary

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significantly depending on the process employed (Janhoappliedm et al., 2009). This water must be disposed off or safely treated for reuse, which is often costly and problematic for most breweries (Simate et al., 2011), though water reuse is not common in this type of industry, due to the public perception and possible product quality deterioration problems (Janhoappliedm et al., 2009). However, many brewers are still searching for ways to reduce consumption of water during processing and low cost effective treatment of effluent for reuse (Simate et al., 2011).

Currently, among the brewing industries in Kenya, only one is engaged in anaerobic digestion of the waste water with little biogas being produced. The other brewing industries discharge their untreated waste water to the municipal line, which in turn increases its loading. Efforts should be made towards providing waste water treatment options for these industries to allow environmentally friendly disposal of their waste water with potential for bioenergy production.

Waste water characteristics play an important role in the selection of treatment process of the waste water (Rana et al., 2014; Ojoawo et al., 2015). Biological oxygen demand (BOD_5), Chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), total nitrogen and phosphorous are some of the physicochemical parameters used to characterize waste water (Shivsharan et al., 2013). BOD_5 measures the amount of oxygen required by bacteria for breaking down to simpler substances, the decomposable organic matter present in any water, wastewater or treated effluent. It is a measure of the concentration of organic matter present in any water. The greater the decomposable matter presents, the greater the oxygen demand and the greater the BOD_5 values (Wolfgang et al., 2012; Singh et al., 2012). COD is a measure of the total quantity of oxygen required to oxidize all organic material into carbon dioxide and water. The COD values are always greater than BOD_5 values. The BOD_5 to COD ratio is commonly used as an indicator for biodegradability of the waste and is dependent on the characteristics of the waste. Standard values for BOD_5/COD biodegradability index for different types of wastewater were scanty in literature. However, reported values for biodegradability index vary from 0.4 to 0.8 for municipal raw wastewater and can exceed 10 for industrial waste water (Samudro & Mangkoedihardjo, 2010; Wolfgang et al., 2012; Zaher & Hammam, 2014). However C/N/P is also an important parameter for the successful anaerobic degradation of organic wastes.

This study focused on characterizing untreated brewery waste water using physicochemical parameters. The main objective was to evaluate the variations in the quality characteristics of the untreated brewery waste water from different processing streams within the industry prior to treatment with a view of assessing its potential for utilization in biogas production.

2 Materials and methods

2.1 Sample collection and preservation

Waste water was collected from two different brewing industries (hereinafter referred to as 1 and 2) in Kenya at different times. The samples were collected in 2l glass sampling bottles. The bottles were pretreated by washing with 70% ethanol and later rinsed with distilled water and dried overnight in an oven at 105°C, for disinfection and drying of the sampling bottles (APHA, 2005; World Health Organization, 2008). The sampling points included the brewing line; clean in place (CIP) and the mixing point between brewing line and CIP as illustrated in Figure 1. All the samples were stored at 4°C without further treatment, until they were analyzed.

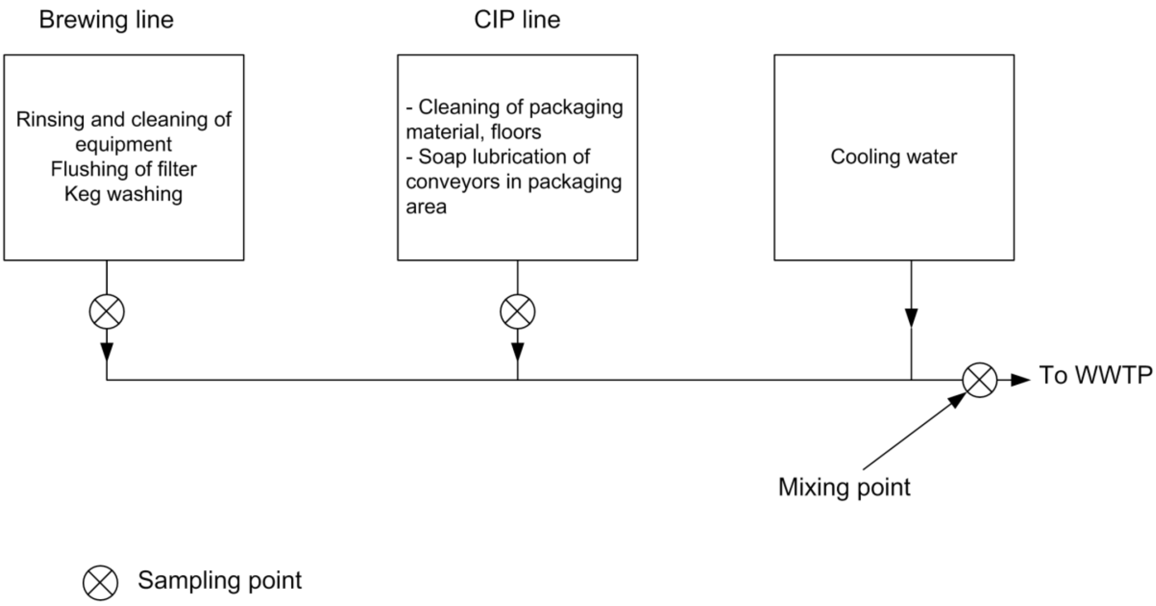

Figure 1 Sampling points

2.2 Laboratory analysis

Analyses of the samples were all carried out at Kenya Industrial Research and Development Institute Laboratories, Nairobi, Kenya. The samples were analyzed as per standard method for the examination of water and wastewater and triplicates of the samples were used (APHA, 2005). The physicochemical characteristics measured include: BOD_5, COD, TDS, TSS, TS, sodium, total nitrogen and total phosphorous.

2.2.1 Total solids (TS), total dissolved solids (TDS), total suspended solids (TSS)

Total solids were determined by gravimetric method and then total suspended solids were calculated by using the following Equation 1

$$TS = TSS + TDS \tag{1}$$

2.2.2 Biochemical oxygen demand (BOD)

BOD was estimated by preparing required volume of dilution water with the addition of nutrients namely phosphate buffer, magnesium sulfate, calcium chloride and ferric chloride. The diluted sample was transferred to BOD bottles. After determining initial DO, final DO was estimated of the bottles kept for incubation period of 5 d. The bottles kept for DO determination and blank were fixed by adding 2 mL manganese sulfate ($MnSO_4$), 2 mL of alkali iodide azide

2.2.3 Chemical oxygen demand (COD)

COD determination was carried out with dichromate reflux method with the addition of 10 mL of 0.25 N potassium dichromate ($K_2Cr_2O_7$) and 30 Ml $(H_2SO_4 + Ag_2SO_4)$

reagent in 20 mL diluted sample. The mixture was refluxed for 2 h and was cooled to room temperature. The solution was then diluted to 150 mL by using distilled water and excess $K_2Cr_2O_7$ remained was titrated with ferrous ammonium sulfate (FAS) using ferroin indicator.

$$COD = \frac{((A-B)\times N \times 100 \times 8)}{V\ of\ Sample} \tag{2}$$

Where *A* is the volume of FAS used for blank, mL; *B* is the volume of FAS used for sample, mL; *N* is the normality of FAS; 8 is milli equivalent weight of oxygen; and *V* is the volume of sample.

2.2.4 Total nitrogen

The nitrogen levels were determined using Kjedhal Method, where the sample was weighed, digested, neutralized and the nitrogen estimated by titration.

2.2.5 Sodium

The sodium levels were determined using Atomic Absorption Spectrophotometer equipment (AAS). Prior to measurement, the sample were digested in 1:1 HCL on a sand bath. After digestion, distilled water was used to take to mark and the sample subjected to AAS.

2.2.6 Phosphorous

The phosphorus levels were determined using UV spectrophotometer. Prior to measurement, the samples were digested in 1:1 HCL on a sand bath. After digestion, distilled water was used to take to mark and a complex reagent (molybdate) added and color change was observed. The sample was then read on the instrument.

2.3 Statistical analysis

All the tests were carried out in triplicates and data was analyzed using SPSS version 21 Genstat 12th edition. The single linkage (nearest neighbor) based on Euclidean distances was used to display the clusters for the physicochemical parameters combined at each stage and the distances at which this merger takes place. Computation of hierarchical clustering and heat map of the datasets were carried out using R programming language and Vegan package (R Development Core Team, 2011).

3 Results and discussions

3.1 Variation in the sampling points in the industries

Table 1 shows the means of physicochemical parameters of the untreated brewery waste water regardless of the industry from which the sample was taken. Samples from the brewing line had the highest concentrations for all the parameters measured except sodium concentrations and were significantly different (p<0.001) in concentration levels from the rest of the sampling points. The levels of COD were found to be very high with levels reaching 50,966±20,146.67 at brewing line. The BOD, nitrogen, TS, TDS and TSS followed a trend in which the brewing line had the highest concentrations followed by the mixing line and lastly clean in place line. The concentrations for these parameters were found to be significantly different from each other.

3.2 Interaction between sampling point and the industry

From Table 2, COD levels for brewing line for Industry 1 had the highest value which was significantly (p<0.001) different from those of brewing line for Industry 2, CIP and mixing lines for both industries. COD levels for Industry 2 brewing and mixing lines were not significantly different from each other; while the levels of CIP in both industries and Industry 2 mixing line were found to be not significantly different from each other. BOD results indicated that there were significant differences in values obtained, between the industries and sampling points, with the exception of brewing line for industry 1 and mixing line for Industry 2, which were not significantly different from each other. The TDS concentration at CIP line for Industry 1 and brewing line for Industry 2 were not significantly different from that at CIP line for Industry 2 (Table 2). Similarly, the phosphorous concentration levels at brewing line for Industry 2 was not significantly different (p<0.001) from that at CIP line for the same industry. Generally, brewing line for Industry 1 had the highest concentrations in all the physicochemical parameters, also supported by Figure 2, a part from sodium which was not significantly different from other sampling lines in these industries with the exception of mixing line in Industry 2.

Table 1 Means for the physicochemical parameters of sampling points

Sampling point	COD	BOD	Nitrogen	Phosphorus	Sodium	Total solid	TDS	TSS
Brewing line	50966±20146.67 [a]	3403±53.52 [a]	196.23±53.52 [a]	81.54±33.94 [a]	17.7±3.35 [b]	19546±7120.59 [a]	14135±5891.45 [a]	5411±1235.4 [a]
CIP line	3610±541.51 [b]	1170±348.83 [c]	11.2±348.83 [c]	5.92±0.97 [b]	44.3±13.22 [b]	1216±126.78 [c]	1053±92.83 [c]	163±47.5 [c]
Mixing line	2167±61.46 [c]	2812±307.9 [b]	18.2±307.9 [b]	4.74±2.04 [b]	370.2±133.67 [a]	2157±261.63 [b]	1521±16.53 [b]	636±245.16 [b]
LSD	1035	64.1	3.498	3.407	35.93	142.2	157.5	251.1
CV%	4.4	2.1	3.7	8.8	19.8	1.5	2.2	9.6
p value	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Note: LSD means least significant difference; CV means coefficient of variance.

Table 2 Means for the physicochemical parameters of sampling point and industry

Point & Industry	COD	BOD	Nitrogen	Phosphorus	Sodium	Total solid	TDS	TSS
Brewing 1	96000±1154.7 [a]	3500±57.74 [a]	359.33±3.37 [a]	157.33±3.71 [a]	10.2±0.21 [b]	35467±156.78 [a]	27308±162.81 [a]	8159±275.33 [a]
Brewing 2	5931±34.06 [b]	3307±40.55 [b]	33.13±2.03 [b]	5.75±0.87 [bc]	25.2±0 [b]	3625±26.09 [b]	963±17.33 [cd]	2662±9.17 [b]
CIP 1	2133±66.67 [c]	390±0 [e]	11.2±0 [c]	8.1±0 [b]	73.9±0.08 [b]	1499±6.67 [d]	1249±64.92 [bc]	249±61.33 [d]
CIP 2	2200±115.47 [c]	1950±0 [d]	11.2±0 [c]	3.75±0 [bc]	14.7±0 [b]	933±15.25 [e]	857±17.98 [d]	76±3.06 [d]
Mixing 1	2400±38.68 [c]	2123±14.53 [c]	28±0 [b]	9.27±0.38 [b]	74.1±0.12 [b]	1572±4.93 [d]	1484±2.96 [b]	88±6.23 [d]
Mixing 2	4820±11.84 [b]	3500±0 [a]	8.4±0 [c]	0.2±0 [c]	666.3±40.39 [a]	2742±0 [c]	1558±0 [b]	1184±0 [c]
LSD	1463.7	90.6	4.946	4.818	50.81	201.1	222.7	355.1
CV%	4.4	2.1	3.7	8.8	19.8	1.5	2.2	9.6

Note: LSD means least significant difference; CV means coefficient of variance.

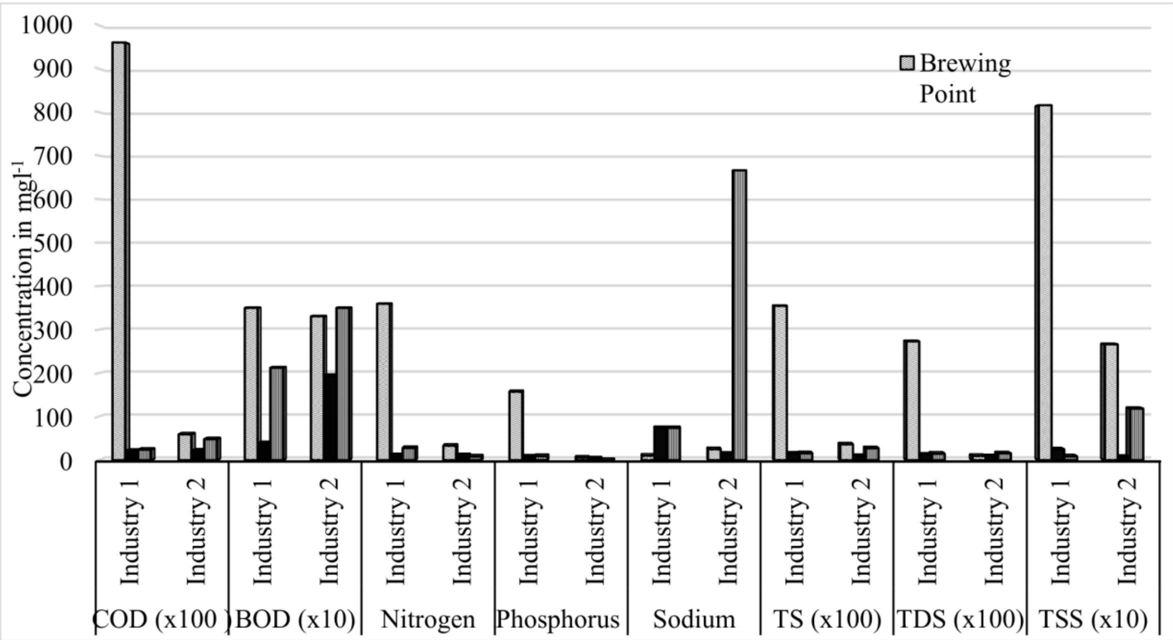

Figure 2 Interaction between sampling point and industry for physicochemical parameters measured

Generally, the brewery wastewater in this study was characterized by large variations in the parameters mentioned in Tables 1 and 2 and Figure 2. The high values of chemical oxygen demand (COD) in the brewery wastewater from all the industries indicates heavy load of organic components (sugars, soluble starch, ethanol, volatile fatty acids, etc.). The values of COD levels at the mixing line are comparable to the obtained values in literature of 2000 mg/L to 6000 mg/L (Caliskan et al., 2014; Simate et al., 2011). The discharge of this wastewater to the environment without any treatment would play a significant risk for public health and environmental pollution. High BOD levels could accelerate bacterial growth which consumes the oxygen levels when discharged untreated into the river. The oxygen may be diminished to levels that are lethal for most fish and many aquatic insects (Akpor et al., 2011). Nitrogen and phosphorus levels were found to be generally high at the brewing lines for both industries with Industry 1 values being significantly different from that of brewing line for Industry 2. This could be contributed by the difference in the raw material used by these industries for instance barley or rice during brewing (Goldammer., 2008), and differences in fermentation and maturation step and variations in the amount of yeast present in the effluent as reported by Caliskan et al, (2014). The differences in phosphorous levels could also be contributed by heavy use of phosphorous containing chemicals used during cleaning and rinsing of brewing equipment and at the keg washing stage. The total suspended solids were found to be 636mg/L which was slightly higher than the literature values of 600 mg/L.

3.2.1 Hierarchical clustering of the physicochemical clustering

In order to evaluate the similarities (or dissimilarities) of the datasets based on the physicochemical parameters, hierarchical clustering using Bray-Curtis dissimilarity was performed as presented in Figure 1. From the six sampling points, the clean in place for Industry 2 (CIP 2), mixing point for Industry 1 (Mixing1) and clean in place for Industry 1 (CIP 1) were clustered in one group while mixing point for Industry 2 (Mixing 2) and brewing line for Industry 2 (Brewing 2) were shown to form another group. This implies that the sample points clustered together have similar physicochemical attributes hence the waste water from this streams could be mixed prior to treatment without significantly affecting the treatment process. From the six sampling points, brewing line for Industry 1 (Brewing 1) was observed to be distantly related from all the others. Thus the characteristics of waste water at this point have different characteristics in terms of concentration levels from the rest. This could also be attributed to the difference in processing method and raw materials employed by Industry 1 in relation to Industry 2. This was also supported by the heatmap showing the similarities between the sampling points and physicochemical parameters, Figure 2. From the heatmap additional information can also be extracted about the physicochemical parameters. In which case, total solids and TDS were in one cluster while BOD and TSS were in another. This clustering of the physicochemical parameters insinuates similar pattern of concentrations of the parameters across the sampling points. The pattern of concentrations of sodium, total nitrogen and phosphorus were shown to be similar according to the heatmap. COD on the other hand was observed to be an outlier from other parameters as the values obtained for both industries were high implying that this waste water could be digested using anaerobic digestion (Metacalf & Eddy, 2004)

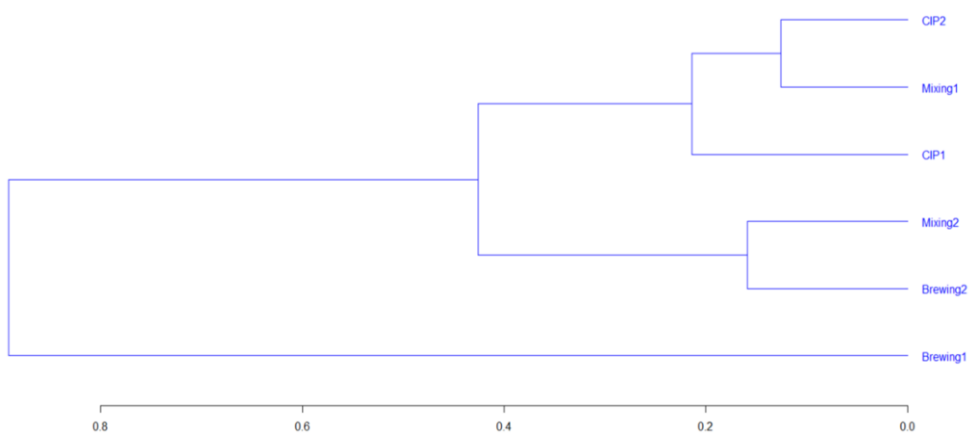

Figure 3 Physicochemical parameter clustering for industries 1 and 2

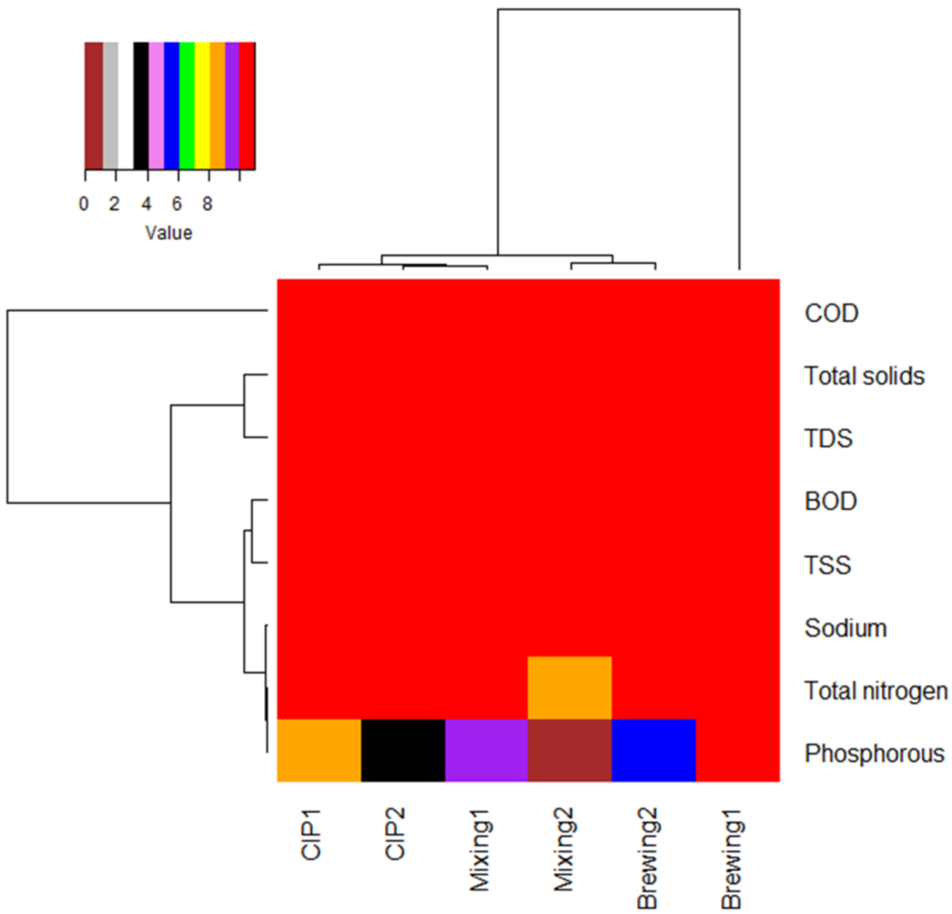

Figure 4 Similarities between the sampling points and physicochemical parameters

A principal component analysis was used to assess the factor composed of the physicochemical parameters measured that best explain the greatest variability in water quality regardless of the industry. The amount of variability explained by the two principal components was 94%, thus the waste water from these industries could best be described using total nitrogen content, total solids, total phosphorus content, TDS, COD , BOD and TSS. These parameters explain the water quality by 76.60%. Sodium and BOD content explained water quality by 16.00%.

3.2.2 Biodegradability of untreated brewery waste water

The study established the BOD to COD ratio of the industries to be 0.039, 0.177, 0.911 for brewing line, CIP line and mixing line respectively for Industry 1 and 0.567, 0.766, 0.766 for brewing line, CIP line and mixing line respectively for Industry 2. In all the two industries the BOD to COD ratio for the brewing line was found to be the least with the mixing point having a range of 0.766 to 0.911. The low values for the brewing line could be attributed to high levels of COD in this line contributed by heavy organic components (Simate et al., 2011). These are close to literature values obtained by Zheng et al., (2015) in which the biodegradability of the influent waste water was found to be about 0.45.

A bivariate correlational analysis was performed to evaluate the level of association between the physicochemical parameters of the two industries. Though there was a 44.4% correlation between COD and BOD, this could not be considered credible as it was not significant. Sodium level did not report a significant correlation with any of the water quality variables evaluated in this study, depicting that an increase or decrease in sodium concentration in the water would not correspond to a significant change in other variables and vice-versa. The highest correlation was between total solids and COD (99.9%), depicting an almost perfect positive relationship between the two parameters. Similarly TDS and TS had a strong association (99.7%) and this relationship was significant at (p<0.001). BOD and TSS had a 58.6% association with each other and the association was significant at p=0.011.

A correlation analysis was also performed to evaluate the level of association between the BOD to COD ratios and the other physicochemical parameters. It was found that an increase in the nitrogen, sodium and total solids levels in the waste water could result to a positive effect on the BOD to COD ratio while an increase in the phosphorous levels would have a negative effect, as per the general model described by:-.

$$Y = 0.533 + 0.033N - 0.025P + 0.00081S + 0.00024TS \quad (3)$$

where Y is BOD to COD ratio and N, P, S, and TS are nitrogen, phosphorous., sodium and total solids respectively.

Since the effect of phosphorous to the ratio was not significant at p<0.05, the model was reduced to:-

$$Y = 0.533 + 0.033N + 0.00081S + 0.00024TS \quad (4)$$

3.2.3 Model validation

The model Equation 4 was used to predict the BOD to COD values as tabulated in Table 3. The sum of squared difference was obtained as 0.530 and a mean squared error of 0.029. The model also explained 73% variations in the BOD_5 to COD ratio (R^2=0.7339).

Table 3 Fitted and experimental values for BOD_5 to COD ratio

B.O.D$_5$/C.O.D	
Experimental value	Fitted value
0.03829787	-0.005915492
0.03469388	-0.089775058
0.03645833	0.180407143
0.17727273	0.406972006
0.17727273	0.402207690
0.19500000	0.406839400
0.85123632	0.890627948
0.89583333	0.915195173
0.90870124	0.925443116
0.55091820	0.480278422
0.55177112	0.642845197
0.56988703	0.793166274
0.88636364	0.605503210
0.81250000	0.593154731
0.97500000	0.597434555
0.72614108	0.6597434555
0.72916667	0.764026128
0.72299112	0.672167216

4 Conclusion

The untreated brewery waste waters generally had high levels of COD and BOD in both industries and the variations were prominent between industries. This could be attributed to difference in processing method, raw materials and chemicals used by these industries. These industries have high organic loadings, thus the demand for environmental investments are high but, the organic material available in brewery wastes also has very high potential for bioenergy production allowing an environmentally friendly disposal solution. However, pretreatment prior to the digestion is unavoidable for improved biogas production. The low ratio of BOD to COD at the brewing line and CIP line, could have a negative effect on the biogas production thus anaerobic digestion of the waste water from these streams separately could be uneconomical.

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