

Wastewater Sampling Methods: Before sampling, the plastic sample bottles cleaned thoroughly using a detergent, 1:1 HCl, triple rinsed with distilled water and during sampling the bottles were triple rinse with the wastewater as suggested by Fatoki and Mathabatha (2001). The Wastewater Treatment Plant (WWTP) of the brewery consists of four main units namely: influent tank, equalization (buffer), anaerobic effluent tank (UASB reactor) and post-aeration tank. The samples were taken at the inlet point of the raw wastewater and an outlet of each treatment unit and at the final discharge point of the treatment plant using 1 L polypropylene bottles from April 2016 to September 2016. Considering the variability of nature of brewery effluent, a snap sampling method was used, and five round (twenty-five) samples of wastewater were taken for the analysis of the selected physicochemical parameters.

Physicochemical Parameters Analysis Methods: Before any analysis of samples, instruments were calibrated using standard solutions. Determinations of the parameters were done according to the analytical methods described in Standard Methods for the Examination of Wastewater (APHA, 2005), using graded laboratory reagents. For all the methods that required the use of the spectrophotometer, both reagent blanks and sample blanks were used.

The PH, temperature Total Dissolved Solid (TDS) and conductivity (EC) of the samples were measured in-situ and Nitrate-nitrogen (NO_3^- N), Nitrite nitrogen (NO_2^- N), Ammonium Nitrogen (NH_4^+ N), Orthophosphate (PO_4^{3-}), Hydrogen Sulfide (H_2S) and sulfate (SO_4^{2-}) were determined using spectrophotometer (HACH DR/5000 Model, Loveland, CO, USA) according to manufacturer's instructions. The TSS was determined by the gravimetric method at a temperature of 103-105 °C according to standard methods of APHA (2005).

The Biological Oxygen Demand (BOD) which is expressed as weight of oxygen consumed per unit volume of water during a defined period (5 days) at a defined temperature (20°C) was calculated following the method of Hamer (1986) and was determined as the difference between initial oxygen concentration in sample and concentration after 5 days incubation in BOD bottles at 20°C. The Chemical Oxygen Demand (COD) was determined by colorimetric determination method using HACH spectrophotometer (HACH DR/5000 Model, Loveland, CO, USA).

Pollutants Removal Efficiency Determination Method: Pollutant removal efficiency of each treatment unit of the plant was evaluated from the difference in

pollutants concentration in the influent and effluent from each unit, using the following formula (Enitan *et al.*, 2015).

$$\text{Removal Efficiency (\%)} = [(C_i - C_e)/C_i] \times 100$$

Where, C_i = is the concentration of the pollutants in the influent; C_e = is the concentration of the pollutants in the effluent.

Data Analysis: The data obtained were analyzed using appropriate statistical tools: Excel spreadsheet and statistical software using Microsoft Excel and SPSS version 16, respectively. One-way ANOVA was performed to assess whether there is a significant difference in the quality of the parameters at every stage of the treatment, significance test was performed at $\alpha = 0.05$. Furthermore, the results from the analysis of physicochemical parameters of the final effluent were compared with recommended industrial discharge limit set by EEPA (2003).

RESULTS AND DISCUSSION

Characteristics of the Raw Wastewater: The determined EC, TDS and turbidity values in this study ranged from 1900.0 to 1921.0 $\mu\text{S/cm}$, 950.0 to 961.0 mg/L and 850 to 1110.0 NTU, respectively (Table 1). These values are within the wider ranges reported for some brewery raw wastewater by Yared (2008) and Kebena (2014). The TSS concentration ranged from 510.0 to 680.0 mg/L with an average value of 606.3mg/L (Table 1) and this was found within the range reported by Driessen *et.al* (2003) and Kebena (2014) for Addis Ababa St. George Brewery in Ethiopia. As described by Brewers of Europe (2002) and Driessen *et.al.* (2003), brewing activities like malt processing and filtration could be the cause for the high TSS values, which indicated that brewery solids mainly of spent grains, Kieselguhr, surplus yeast, cold break and possible label pulp from the bottle washer.

Brewery raw wastewater had COD value ranging from 2510.0 mg/L to 2617.0 mg/L with the average of 2565.7mg/L (Table 1). This COD value was within the range reported by Kebena (2014) (1750 mg/L to 2800 mg/L) and Driessen, *et.al.* (2003) (2000 mg/l to 6000 mg/L). The obtained BOD₅ value ranged from 1303 mg/L to 1620 mg/L with the average value 1460mg/L (Table 1) and it was found that 1331 mg/L to 1991 mg/L and 1200 mg/L to 3,600 mg/L, respectively, was reported by the same authors. As indicated by Enitan *et al.* (2015), the trends and variability of the values plus large standard deviations from the means shows that the pollution level of the raw wastewater is high. Therefore, the observed high value of standard

deviation of BOD seems to be due to the variability of brewery wastewater composition.

According to the Brewers of Europe (2002), the high organic loads in the raw wastewater arise from dissolved carbohydrates, the alcohol from beer wastes, and a high content of suspended solids, such as spent grain, malt, and yeast. It is also explained that the raw materials like malt and adjuncts, and the discharge of trub, weak wort, surplus yeast, emptying and rinsing of process tanks, pre and after- runs of Kieselguhr filtration and drip beer could possibly be the sources of high COD and BOD₅ in the wastewater. Brewers of Europe (2002) also noted that organic components in brewery effluent which have BOD₅/COD ratio of 0.6 to 0.7 are generally easily biodegradable. The present results indicated that the BOD₅/COD ratio was nearly 0.6 (0.57), which is indicative of easily biodegradability nature of organic matter in the raw wastewater.

Results of nutrient load analysis of wastewater (Table 1) showed that the average concentrations of TN, NH₄-N and TP were 61.0 mg/L, 30.9 mg/L and 34.9 mg/L, respectively, and these values were in the range reported by Yared Shumate (2008) and Kebena (2014). According to Brewers of Europe (2002) and Driessen et.al. (2003), the raw materials malt and adjuncts, the nitric acid used for cleaning and the amount of spent yeast present could be the sources of nitrogen in the wastewater. Therefore, sources of the nitrogen forms could be malt processing followed by protein hydrolysis into NH₄-N and NO₃-N. Also, it might have come from dissociation of the nitric acid used in the Cleaning-In-Place (CIP) units as well as ammonification and nitrification of the ammonium nitrogen in the wastewater during the periods of sample collection for analysis. Furthermore, the average concentrations of SO₄²⁻ and H₂S ranged were 6.4 mg/L and 0.6 mg/L, respectively (Table 1). The pH values of wastewater ranged from 12 to 13 pH units which were within the wide range (2-12) pH values given by Driessen et.al. (2003) for the discharges from different sections of a brewery. But Kebena (2014) reported a narrow range of pH (6.2 to 11.8) and this variation could be attributed to the batch processing nature of the brewery and the amount and type of chemicals (e.g. caustic soda, phosphoric acid, nitric acid, etc.) used at the CIP units.

In general, results (Table 1) of the present study revealed that except for temperature (36-38 °C), all of the other analyzed physicochemical parameters values of raw wastewater exceeded the discharge limit set by EEPA (2003). Moreover, the raw effluent produced from the brewery did not meet the discharge limit for

wastewater disposal to water bodies according to the European Union (EU) discharge limits (Driessen and Vereijken, 2003). Therefore, for better environmental protection, the raw wastewater needs to be treated at an acceptable level using efficient treatment system before it is discharged to the environment.

Physicochemical Characteristics and Performance Efficiency of Each Treatment Unit: Before the treated effluent of the factory is released into the surrounding environment, the wastewater passes through four series of treatment units of the WWTP system arranged in the order of influent tank, equalization tank, anaerobic effluent tank (UASB reactor) and post aeration tank. The recorded physicochemical parameters values of each treatment unit (after their respective retention time) are depicted in Table 2. The trend of values of nine parameters (COD, BOD₅, TSS, TN, SO₄²⁻, H₂S, TP, turbidity and temperature) showed a continuous decrease as the wastewater passed through the four units. Pollutant removal of each of the treatment unit is described below.

Influent Tank Removal Efficiency: Large particles, fat, oil and grease are removed by the coarse screen and a static oil trap that is installed at the inlet of the WWTP and then the brewery wastewater is collected in the influent pump pit tank in which it is retained for about 5 minutes. Comparison of the mean value of the parameters in the raw effluent with that in an effluent from the influent tank indicated (Table 2) a significant difference ($p < 0.05$) only for the parameters such as EC, Turbidity and H₂S. The recorded average removal efficiencies of influent tank was 37.54% for SO₄²⁻, 22.93% (TDS), 22.9% (EC), 7.07% (turbidity), 4.90% (TN), 4.01% (TP), 2.4% (temperature), 0.75% (BOD₅), 0.71% (TSS), 0.65% (COD), 0.47% (PH) and -10.7% (NH₄-N) (Table 3). Kebena (2014) reported higher removal efficiencies for Addis Ababa St. Gorge brewery than the present study for BOD₅ (1.67%), TSS (19.64%), COD (5.28%) and NH₄-N (1.98%), and lower efficiencies for TDS (3.05%), TN (1.29%), and TP (0.52%). Results (Table 2) of the present study revealed that the concentration of NH₄-N was increased above that in raw wastewater (from 30.9±7 to 34.2±8.4 mg/L) and consequently decreased in removal efficiency (Table 3). As described by Gerardi (2002), the increment of NH₄-N concentration may be associated with the reduction (de-nitrification) process of NO₃-N into NH₄-N by anaerobic bacteria.

Equalization (Buffer) Tank Removal Efficiency: Before it enters into the UASB reactor, the raw wastewater passes over a static fine screen for mechanical pre-treatment in order to reduce the

amount of suspended solids. Comparison of the average values of effluent from the influent tank with that of the equalization tank showed a significant decrease in pollutants ($p < 0.05$) only for TDS TSS, pH and $\text{NH}_4\text{-N}$ (Table 2). The average removal efficiencies of the tank was 38.85% (PH), 28.5% (TSS), 19.02% (TDS), 18.9% (EC), 10.3% (turbidity), 3.5% (temperature), 2.7% (BOD_5), 2.4% (TP), 1.16% (COD), -9.6% ($\text{NH}_4\text{-N}$) and -30.0% (SO_4^{2-}) (Table 3). Kebena (2014) reported relatively higher removal efficiencies of equalization tank for Addis Ababa brewery than the present study for COD, BOD_5 , SO_4^{2-} and TP and $\text{NH}_4\text{-N}$, but lower efficiencies for TSS and TDS.

Results of the present study revealed that after treatment in equalization tank, the concentration of $\text{NH}_4\text{-N}$ was still increased above that recorded for the influent tank (from 34.2 to 37.5 mg/L) (Table 2) resulting in a decrease in its removal (Table 3). According to Larisa (2008), such decrease in ammonium removal could be related to the involvement of nitrate-reducing bacteria in anaerobic digestion that reduces NO_3^- into ammonium (NH_4^+). In addition, there was a decreased in SO_4^{2-} removal efficiency of the equalization tank and as suggested by Sperling (2007), this may be due to the hydrolysis of protein-based large molecules and complex organic molecules into sugar and amino acids.

According to Gerargi (2003), the concentrations of macronutrients such as phosphate and nitrogen are estimated in relation to COD present in the wastewater. It is also recommended that the ratio of COD: N: P should be maintained at 350: 5: 1, since a deficiency of some of these nutrients in the wastewater may cause a deficiency in the growth of the bacteria involved. The results obtained in this study revealed that the ratio of COD: N: P was 77: 1.7: 1, indicating there was still higher concentration of nutrients in the wastewater that is released from equalization tank and entering to the proceeding biological treatment unit (UASB reactor).

According to Stephenson and Blackburn (1998), an increase in the organic concentrations can be explained by the fact that the lime used in pH correction could have also acted as coagulants, thereby improving the settling properties of the solids. According to Spellman (2003), the BOD_5 removed efficiency of primary effluent treatment plant should be 25-35mg/L. However, the result (Table 2) obtained from this study was found to be 40 mg/L, which shows the effectiveness of the primary effluent treatment units.

Anaerobic Effluent Tank (UASB reactor) Removal Efficiency: Pre-treated wastewater is fed into UASB reactor, where most biological treatment expected to takes place. The retention time in the UASB reactor was 6 hours. After the wastewater passed over the UASB reactor, the values of most pollutants decreased and comparisons of the mean value measured in this unit with equalization tank indicated significant differences ($p < 0.05$) for EC, TDS, TSS and turbidity (Table 2). The high BOD_5 (94.6%), COD (91.2%) and TSS (78.9%) removal efficiencies recorded (Table 3) in the UASB reactor of Hawassa brewery is almost consistent with that reported by Kebena (2014) for Addis Ababa brewery and also it is within the ranges that reported by Sharda et.al. (2013) for M/s Carlsberg India Ltd brewery industry in India. The high BOD and COD removal efficiencies of UASB reactor observed in this study may be due to properly kept operational parameters of the reactor and its organic loading rates. The BOD/COD ratio ranges from 0.3-0.4 due to the fluctuations in inflows, quantity and quality of the effluent and is a function of various processes like brewing, fermentation and clarification, etc. Although settleable solids are often a problem in breweries, as described by (Sharda et.al. (2013), the observed TSS removal efficiencies of 78.9% (Table 3) may be attributed to the higher Volatile Suspended Solids (VSS) resulting in the formation of granular sludge bed in the UASB reactor.

Similarly, high removal efficiencies of 80.84% and 80.8% were recorded in this study (Table 3) for EC and TDS, respectively and this is much higher than the 28.94% (EC) and 26.28% (TDS) reported by Kebena (2014) for Addis Ababa brewery. These high removal efficiencies may be due to the proper functioning of the reactor. Relatively lower removal efficiencies were recorded for nutrients such as TP (20.2%), SO_4^{2-} (19.2%), $\text{NH}_3\text{-N}$ (14.7%) and TN (14.3%) (Table 3). However, these are higher than the 1.45%, 5.86%, -9.5% and 1.92%, respectively, reported by Kebena (2014). Moreover, the treatment efficiency of the UASB reactor obtained in this study was 38.85%, 10.7% and 10.3% for pH, temperature and turbidity, respectively (Table 3).

Post Aeration Tank Removal Efficiency: After treatment in UASB reactor, the anaerobic effluent flows to the post-aeration tank where it is post-aerated in order to remove odor compounds mainly H_2S from the anaerobic effluent and further reduction of organic matter. Comparisons of mean differences of pollutant in an effluent from UASB reactor with effluent from the post-aeration tank reactor, there were significant differences ($p < 0.05$) for TSS, temperature and $\text{NH}_4\text{-N}$ (Table 2).

Throughout the treatment units, the concentrations of H₂S (Table 2) has increased indicating poor H₂S treatment of the plant. This seems to be due to lack of sufficient hydraulic retention time (HRT) of the effluent in the aeration tank. According to Bosnic *et al.* (2000), H₂S is a soluble gas and can form weak acids that can cause corrosion and in sewer lines, it can affect structural reinforcements and corrode pipe works. Thus, any discharge to water bodies, even with low concentration can pose toxicological hazards.

The TDS discharge limit set by EEPA (2003) is 80 mg/L and the result obtained from the study had mean value 110.6±0.6mg/L (Table 4), which is above the limit. The source of high ionic strength and consequent high TDS is expected to be due to chemicals (such as NaOH, H₂SO₄, HNO₃, H₃PO₄) used by the factory as a cleaning agent. Even though the overall removal efficiency of TDS is higher (92.0%), findings of the present study revealed that the treatment system of Hawassa brewery is not effective enough to bring the concentration below the discharge limit.

Conclusion: Findings of the present study revealed that raw wastewater of the factory had higher values of physicochemical parameters, which were above the national industrial discharge limits. In most cases, the values decreased as the wastewater passed over the treatment units of the plant indicating the involvement of the units in the removal of pollutants, although their efficiencies vary greatly. The study revealed that the values of some nutrient namely: TN, TP, H₂S and TDS were higher than the discharge limits indicating the Hawassa St. Gorge brewery waste treatment plant is not effective enough to lower concentrations of these parameters below the discharge limit. If discharged to the surrounding environment directly, some of these nutrients would have an adverse effect on the environment and human health, as the effluent directly joins a stream, river and finally lake Hawassa. Therefore, to make the plant more efficient, the factory must take some technological and technical measures, for example, integrating the UASB treatment system with aerobic fluidized bed reactor. Furthermore, as the treated effluent contains nutrients, it can be recycled for non-potable uses such as irrigation of garden in the factory, etc, which may reduce the amount effluent discharged and reduce the dependence of the factory totally on fresh water supply for all activities. Moreover, the methane-rich biogas from UASB reactor may be used as a fuel for different activities including boiler. Also, the factory should take measures to reduce odor emission, as people living in the surrounding complain bad smell from the effluent. As brewery effluent quality is variable, more similar

studies and monitoring should be carried out for the important parameters.

Acknowledgements: We would like to thank BGI Hawassa St. Gorge brewery office and members of management body for financial support and the experts working at WWTP for technical support during the study period. We also would like to acknowledge S/N/N/P Regional Water Resource Bureau for allowing to use their laboratory for analysis.

REFERENCES

- Alebel, A. (2014). Does ISO 14001 accreditation reduces environmental impact of industries: A case study in Addis Ababa, Ethiopia. *Open Journal of water pollution and treatment*, 1(1): 21-33.
- APHA (American Public Health Association).(2005). *Standard Methods for the Examination of water and wastewater*, 24th Ed., Washington, D. C.
- Arcadio, P; Gregoria, A.(2002). *Physical-Chemical Treatment of water and wastewater*. Morgan State University, Department of Environmental, Baltimore, Maryland.
- Bosnic, M; Buljan, J; Daniels R.P. (2000). *Pollutants in tannery effluents*. Report for United Nations Industrial Development Organization (UNIDO) US/RAS/92/120, Regional Programme for Pollution Control in the Tanning Industry in South-East Asia, 9 August.
- Brewers of Europe. (2002). *Guidance Note for Establishing BAT in the Brewing Industry*, Brewers of Europe, Brussels. <http://www.brewersofeurope.org/asp/publications/publications.asp>
- Driessen, W; Vereijken, T;Paques, B. (2003). *Recent Developments in Biological Treatment of Brewery Effluent*. Institute and Guild of Brewery of Africa Sector. Proceeding 9th Brewing Convention, Victoria Falls, Zambia, Netherlands.
- EEPA (Ethiopian Environmental protection Authority). (2003). *Guideline Ambient Environment Standards for Ethiopia*. Prepared by EPA and UNIDO under ESDI project US/ETH/99/068/ Ethiopia. Addis Ababa.
- Enitan, A;Adeyemo, J;Kumari, S; Swalaha, FM;Bux, F. (2015). *Characterization of Brewery*

- Wastewater Composition International. *Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering*, 9 (9): 1073-1076.
- Fatoki, OS;Mathabatha, S. (2001). An assessment of heavy metal pollution in the East London and Port Elizabeth harbours, *Water South Africa*, 27(2): 233-240
- Gerardi, MH. (2002). *Nitrification and Denitrification in the activated sludge process*. John Wiley and Sons, Inc., New York.
- Gerardi, M. (2003). *The microbiology of Anaerobic Digesters*. Wiley-Inter-science, New Jersey, 51-57.
- Gujer, W; Hanze, M; Mino, T; Matsuo, T;Wentzel, MC;Marais, GR. (1995). Activated sludge Model No. 2: Biological phosphorus removal. *Wat. Sci. Tech.* 31(2): 1-11.
- Hamer, MJ. (1986). Lab chemical analysis in water and wastewater technology. 2nd Ed. Wiley and Sons. New York. pp 30-46.
- Jasa, PJ; Skipton, S; Varner, DL; Hay, D. (1998). G96-1279 Drinking water: nitrate-nitrogen. Historic materials from University of Nebraska-Lincoln Extension.1424
- Kanagachandran, K;Jayaratne, R.(2006). Utilization potential of brewery wastewater, *J. Institute of Brewing*, 112 (2): 92–96.
- Kebena B. (2014). Treatment and Biogas Production Performance Efficiency of St. George Brewery Full Scale Wastewater Treatment System, MSc thesis, Center for Environmental Science, Addis Ababa University, Addis Ababa, Ethiopia.
- Larisa, K. (2008). Anaerobic Treatment of Wastewater in a UASB reactor. Licentiate Thesis in Chemical Engineering, Department of Chemical Engineering and Technology. Division of Chemical Engineering, Royal Institute of Technology Stockholm, Sweden.
- Marx, DH.(1995). Application of municipal sewage sludge to forest and degraded Land. "Agricultural utilization. Urban and Industrial by-products". ASA, special publication,58, USA.
- Sharda, AK; Sharma, MP; Kumar, S. (2013). Performance Evaluation of Brewery Waste Water Treatment Plant. *International Journal of Engineering Practical Research (IJEPR)*, 2 (3): 105– 111.
- Spellman, FR. (2003). *Handbook of water and wastewater treatment plant operations*.CRC Press LLC.
- Sperling, MV. (2007). Wastewater characteristics, treatment and disposal. IWA Publishing.
- Stephenson, R;Blackburn, JB.(1998). *Industrial Wastewater Systems Handbook*. Lewis Publishers, USA.
- Teixeira, ST;Melo, WJ;Silva, ET. (2005). Heavy metals in a degraded soil treated with sludge from water treatment plant. *Sci. Agric.* 62 (5): 498-501
- Yared, S. (2008). Biological Nutrient Removal from Brewery Wastewater using a Laboratory Scale Anaerobic/Anoxic/Aerobic Bioprocess. MSc thesis, Center for Environmental Science, Addis Ababa University, Addis Ababa, Ethiopia.