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# Trace metals analysis in wastewater discharged from Debre Berhan Dashen Brewery

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**Abstract**

**The efficiency of wastewater treatment plant of most industries in Ethiopia is under question. Thus, this study aimed at to evaluate heavy/trace metals analysis in wastewater discharged from Debre Berhan Dashen Brewery. Wastewater samples were collected from the influent and outlet of each treatment unit and from the outside where farmers uses the effluent for irrigation purpose. Heavy metals were analyzed by ICP-OES. The results revealed that all heavy metals analyzed except Mercury (Hg) and Molybdenum (Mo) were below the permissible limit. Mercury (Hg) was found 0.05±0 mg/L and Molybdenum (Mo) was found 0.015±0.1 mg/L.**

**Keywords: Heavy metals, Dashen Brewery, Wastewater.**

## 1. Introduction

Environmental pollution mainly arises from discharge of treated or untreated industrial wastes to the environment[1–3].In Ethiopia, the large and medium scale manufacturing sub-sectors are dominated by four consumer goods producing industrial groups, i.e., food and beverage, chemical, textile, leather and shoe groups are the main industrial sectors that contribute to environmental impact [2].Breweries are the conventional industries in agro and food sector using cost effective techniques to manufacture the best quality beer. During the process of beer brewing, beer mainly passes through three very important chemical and bio-chemical reactions (mashing, boiling, fermentation and maturation) and three solid–liquid separations (wort separation, wort clarification and rough beer clarification)[3].Wastewater is one of the major waste products of brewery operations. Brewery consumes large volumes of water and at the same time it also discharges large volumes of effluent throughout the processes. It has been estimated that approximately 3 - 10 L of wastewater is generated per litre of beer produced in breweries[4].

The wastewater treatment system employed at Debre Berhan Dashen Brewery is UASB (up-flow anaerobic sludge blanket) with re-aeration system. A prerequisite for successful operation of a UASB system is the presence of well-settling (granular) sludge, which can stand the up-flow velocity of the wastewater and is retained in the reactor. In the UASB processes, the wastewater to be treated is introduced in the bottom of the reactor. The waste water flows upward through a sludge blanket which is made of biologically formed granules. Treatment occurs as wastewater contact with granules. The gases produced under anaerobic conditions mainly methane and carbon dioxide cause internal circulation, which helps in the formation maintenance of the biological granules. The free gas and the particles with the attached gas rise to the upper part of the reactor. The retention time in the UASB tank is 6 hours at average flow with volume of 700m$^3$.

The treated effluent from the system is released through canal and used by many farmers around Dashen area for irrigation purpose before mixing to tributary of Beresa River. The total time the wastewater spent in the system is 8-9 hours. Heavy metals are elements of high molecular masses, most of which belong to the transition elements [5].Studies have shown that soils of refuse dumpsite contain different kinds and concentrations of heavy metals. In recent times, it has been reported that these elements accumulate and persist in soils at an environmentally hazardous levels [6].This research attempts to evaluate the concentration of heavy metals in the wastewaters released from Dashen Brewery after treatment and the farmers used it for irrigation purpose.

## 2. Materials and Methods

### 2.1. Materials

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The materials which were used during conducting this study are polypropylene bottles for collecting the brewery wastewater samples, incubator, Digital pH meter, ICP-OES (Inductive Coupled Plasma-Optical Emission Spectrometer), Hot plate digester.

## 2.2. Chemicals and reagents

0.1N and 1.54N sodium hydroxide, 0.1N hydrochloric acid, 0.1N nitric acid, Molybdovanadate reagent, Potassium persulfate pillow, $NO_3$-N/LCK 300 vials, LCK 340A solution. All working solutions were made using high-purity deionized water.

## 2.3. Wastewater sampling and preservation

Wastewater samples were collected from Debre Berhan Dashen Brewery each outlet, while wastewater was discharging into the environment. 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 (SBR). By considering the variability of nature of brewery effluent, a snap sampling method was used. The wastewater samples were collected from the inlet point and an outlet of each treatment unit and at the final discharge point of the treatment plant. Samples were collected between 08:00 and 11:00 AM during the dry season, using a time composite sampling technique using cleaned polyethylene bottles stored in an ice box until transported to the laboratory.

## 2.4. Heavy metals analysis method

The concentration of heavy/trace metals such as Fe, Mn, Cu, Zn, Mo, Ni, Cd, Hg, Pb, As were determined using Inductive Coupled Plasma-Optical Emission spectroscopy (ICP-OES) with radial plasma Observation (model- SPECTRO ARCOS Analytical Instruments, Kleve, Germany) at Horticoop Ethiopia (Horticulture) PLC water and soil laboratory at Bisheftu/Debrezeyit. To ensure the removal of organic impurities from the samples and prevent interferences in analysis, wastewater samples were digested based on the protocol of the American Public Health Association (APHA) [7]. The optimum digestion procedure of waste water samples was according to EPA 3051 with an acid mixture using a hot plate digestion system was as follows. 4 ml of concentrated nitric acid and 1 ml concentrated HCl were added to 50 ml wastewater sample in 250 ml beaker and the mixture was allowed heated on hot plate at 250°C for 3hrs and allowed cool to room temperature, then filtered and transferred to a 50 ml volumetric flask and filled to the mark with double distilled water [8].

# 3. Result and Discussion

## 3.1. Heavy Metal analysis

Crops need trace elements in water for growth processes, but high rates of trace elements concentrations in water can cause plants harm. Copper (Cu) can cause loss of root growth and leaf chlorosis. Zinc (Zn) and Arsenic (As) have significance harm on stem chlorosis and root growth suppression. Aluminum (Al), in acidic soil, can decrease crop productivity. Lead (Pb) and Cyanide (CN) are normally strictly restricted since, when dissolved in water or soil, they accumulated by time in the crop and causing harmful to the human. Molybdenum, nontoxic to plants; can be toxic to livestock if forage is grown in soils with high molybdenum.

Table-1 Mean concentration of trace metals in the wastewater and standard limits

| Heavy Metals | Mean conc.(mg/L) | WHO limits(mg/L) | US EPA limits(mg/L) |
|---|---|---|---|
| Molybdenum(Mo) | 0.015±0.01 | 0.01 | 0.01 |
| Arsenic(As) | 0.04±0 | 0.1 | 0.1 |
| Lead( Pb) | 0.575±0.005 | 5 | 5 |
| Cadmium(Cd) | ND | 0.01 | 0.01 |
| Mercury(Hg) | 0.05±0 | 0.001 | 0.001 |
| Nickel(Ni) | 0.03±0 | 0.2 | 0.2 |
| Iron(Fe) | 1.81±0.6157 | 5 | 5 |
| Copper(Cu) | 0.027±0.005 | 0.2 | 0.2 |
| Zinc(Zn) | 0.84±0.2005 | 2 | 2 |
| Manganese (Mn) | 0.0525±0.0236 | 0.2 | 0.2 |

As indicated in table-1below, the mean concentration of all heavy and trace metals of the sample collected were below the standard limits set by WHO (World Health Organization) and US EPA (Environmental Protection Agency) except Mercury (Hg) and Molybdenum (Mo).

The mean concentration of Hg of the brewery wastewater samples for irrigation purpose was 0.05±0 mg/L, which is above the standard limit given by both WHO and US EPA (0.001mg/L).The mean concentration of Mo of the brewery waste water for irrigation purpose was 0.015±0.1 mg/L, which is slightly above the standard limit given by both WHO and US EPA (0.01mg/L).Since Mercury (Hg) & Molybdenum (Mo) were found above the permissible limit the brewery wastewater has a great effect on the irrigation.

3.2. Method Validation Process

3.2.1. Method Detection Limit (MDL)

The general accepted definition of MDL is the concentration that gives a signal three times the standard deviation of the blank of backgrounds signal.

**Table 2.** Results of IDL and MDL for the brewery wastewater

| Metals | MDL(mg/kg) | IDL(mg/kg) | Wavelength(nm) | Regression Coefficient (R2) | Range(mg/kg) |
|---|---|---|---|---|---|
| As | 0.013 | 0.012 | 189.042 | 0.999 | 0.0012 - 3.84 |
| Pb | 0.0007 | 0.0007 | 220.353 | 0.999 | 0.0007 – 1.68 |
| Zn | 0.0009 | 0.0009 | 213.856 | 0.999 | 0.0009 - 3.36 |
| Cu | 0.0027 | 0.0025 | 214.438 | 0.999 | 0.0025- 3.36 |
| Fe | 0.0019 | 0.0018 | 184.950 | 0.999 | 0.0018 - 4.8 |
| Mn | 0.0004 | 0.0002 | 324.754 | 0.999 | 0.0002 - 4.8 |
| Cd | 0.0002 | 0.0001 | 231.604 | 0.999 | 0.0001 - 1.68 |
| Ni | 0.0009 | 0.0007 | 259.941 | 0.999 | 0.0007 - 1.68 |
| Hg | 0.0028 | 0.0028 | 257.611 | 0.999 | 0.0028 - 3.84 |
| Mo | 0.0003 | 0.0003 | 202.095 | 0.999 | 0.0003- 1.20 |

To determine MDL value nine replicates were analyzed and blank was spiked with respective analyte and calculated as follows [9].

$$MDL = SD \times t$$

Where:
MDL- method detection limit
SD- standard deviation of measured replicates
t- Student's t- value measured at 99% confidence level (In this particular case N=9, t=2.821)

3.2.2. Instrumental Detection Limit (IDL)

Instrumental detection limit (IDL) is the smallest quantity of an analyte that can be statistically differentiated from the baseline noise level of an instrument without regard to sample matrix characteristics or to the specific sample preparation and analysis methods employed. The IDL should always be below the method detection limit, and is not used for compliance data reporting. IDLs were estimated by taking 10 replicate measurements of the calibration blank (3%nitric acid). The IDL was calculated to be the concentration equal to three times the standard deviation of those replicate measurements, and the exercise was repeated on three days, as specified in Table 2 below.

3.2.3. Recovery

One of the most important quality assessment tools is testing the recovery of a known addition or spike of analyte to a method blank, field blank or sample. In situations where of standard reference materials are not available it is common practice to perform spiking experiment to evaluate the efficiency of an acid digestion method. Performance of the selected digestion method for water sample measured by conducting recovery test on spiked samples using composite standard solution of the analyzed metals. Percent recovery for the metals was calculated using the following equation [10].

$$\frac{cs-c}{s} X100$$

Where:
R- percent recovery.
Cs- measured concentration of a metal in the spiked sample.
C- Average concentration of the metals in the samples (wastewater or sediment)
S- Concentration equivalent added to the spiked samp

Table 3. Determination of percent recovery of wastewater sample (Influent)

| Metals/Elements | Cs(ppm) | C (ppm) | S(ppm) | %Recovery |
|---|---|---|---|---|
| Molybdenum(Mo) | 0.99 | 0.03 | 1 | 96 |
| Arsenic(As) | 0.98 | 0.04 | 1 | 94 |
| Lead( Pb) | 1.01 | 0.06 | 1 | 95 |
| Cadmium(Cd) | 0.92 | ND | 1 | 92 |
| Mercury(Hg) | 1.01 | 0.05 | 1 | 96 |
| Nickel(Ni) | 1.02 | 0.03 | 1 | 99 |
| Manganese (Mn) | 1.02 | 0.06 | 1 | 96 |
| Iron(Fe) | 3.11 | 2.17 | 1 | 94 |
| Copper(Cu) | 0.97 | 0.03 | 1 | 99.4 |
| Zinc(Zn) | 6.04 | 1.05 | 1 | 94 |

Conclusions

The brewing process uses large volumes of water mostly for the brewing, rinsing and cooling purposes. At same time it also generates large amounts of wastewater effluent and solid wastes. The results of this study also revealed that the treated wastewater of Debre Berhan Dashen brewery has high sodium ion concentration which indicates high salinity of water in nature. Mercury (Hg) and Molybdenum (Mo) were found above the standard given by WHO and US EPA. Due to the high level of these two heavy metals the brewery wastewater is not recommended for irrigation purpose. Thus, the industry needs to improve the performance of the treatment plant of the wastewater so as to use the effluent for agricultural purpose.

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