



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 ± 0.1 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, manufacturing sectors are dominated by four goods producing industrial groups, these are chemical, textile, leather and shoe, food and beverage groups are the major industrial sectors which contribute to environmental impact [2]. Among food and agro sectors, Breweries are the conventional industries having cost effective systems to produce the quality of beer. During brewing process, beer passes commonly through three very important bio-chemical and chemical reactions (boiling, mashing, fermentation and maturation) and three solid–liquid separations (wort clarification wort separation, and rough beer clarification)[3]. In process of beer production, wastewater is the major waste product. Brewery industries use large amount of water and throughout the process it releases large volumes of effluent. It has been projected that nearly three to ten liters of wastewater is discharged for the production of one liter of beer[4].

The wastewater treatment plant implemented at Debre Berhan Dashen Brewery is UASB (up-flow anaerobic sludge blanket) with re-aeration system. The presence

of well-settling (granular) sludge is a prerequisite for effective procedure of a UASB system that can stand the wastewater up-flow rate and retained in the reactor. In the processes UASB, the wastewater is entered in the lower parts of the reactor to be treated. Then the wastewater flows upward through a sludge blanket which is made of biologically formed granules and treatment occurs by way of wastewater contact with granules. Mostly the production of carbon dioxide and methane gases under anaerobic conditions results internal circulation, which helps in the formation maintenance of the biological granules. The adsorbed gas particles and the free gases 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 waste water released from the system through canal is used by the surrounding farmers for irrigation purpose around Dashen brewery area before the waste mixing to tributary of Beresa River. The total time the wastewater spent in the system is 8-9 hours. Current studies have revealed that refuse dumpsite soils contain different kinds and concentrations of heavy metals (transition elements with high molecular masses)[5]. In recent years, researchers reported that heavy metals accumulate and persist for long time in

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soils at hazardous levels for the environment[6]. This study evaluated the heavy metals level in the wastewaters released from Dashen Brewery after treatment.

2. Materials and Methods

2.1. Materials

The materials used to carry out this study were polypropylene bottles for brewery wastewater samples collecting, 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, NO₃-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 each outlet of the Brewery during discharging of wastewater into the environment. The brewery Wastewater Treatment Plant (WWTP) consists of four major units: influent tank, equalization (buffer), anaerobic effluent tank (UASB reactor) and post-aeration tank (SBR). By considering the inconsistency 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 from the final discharge 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 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.

Samples of wastewater were digested in accordance with the American Public Health Association's (APHA) protocol to ensure the elimination of organic contaminants from the samples and avoid interferences in analysis[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 transferred to a 50 ml volumetric flask after filtration and adjusted to the mark with distilled water [8].

3. Result and Discussion

3.1. Heavy Metal analysis

It is known that crops need trace elements for their growth processes, however higher concentration of these elements can cause plants destruction. For instance in acidic soil, Aluminum (Al) can decrease productivity of crop. Copper (Cu) can cause loss of root growth and leaf chlorosis. Zinc (Zn) and Arsenic (As) have significance damage on the stem chlorosis and root growth suppression. Cyanide (CN) and Lead (Pb) must not exist in the plant since, when they are dissolved in water or soil, they accumulated through time in the crop and are harmful to the human beings. The accumulation of Molybdenum may be nontoxic to plants; but it is 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

Metals	MDL(mg/kg)	IDL(mg/kg)	Wavelength(nm)	Regression Coefficient (R ²)	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

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

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

$$\text{MDL} = \text{SD} \times t$$

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 lowest quantity of the analyte that can be statistically distinguished from the baseline noise level of an instrument without respect to sample matrix characteristics or to the specific preparation of the sample and analysis methods used. 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

Testing the recovery is the common quality assessment tools done by addition of known concentration or spike of analyte to a blank, field blank or sample. When there are no standard reference materials, it is a common to carryout spiking experiment to assess the efficiency of an acid digestion method. The performance of sample digestion method was measured by conducting recovery test on spiked samples using composite standard solution.

Percent recovery for the metals was calculated using the following equation [10].

$$\frac{CS-C}{S} \times 100$$

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 sample

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

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4. Conclusions

In the brewery industry large amount water is used for the brewing process, cooling and rinsing purposes. It also produces large volume of wastewater effluent and solid wastes throughout the process. 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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