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Characterization of Brewery Wastewater for Irrigation Purpose (in case of Bedelle Brewery Share Company, Illubabor Zone, South-west Ethiopia)

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Abstract:- Wastewater reuse is a useful tool in minimizing the amount of wastewater in the environment. Therefore, evaluation of the suitability of untreated and treated wastewater of Bedelle Brewery Share Company for irrigation purpose was made according to its composition and the international irrigation water quality standards. In addition, to classify type of water quality and to evaluate its suitability for irrigation purposes: Sodium Adsorption Ratio (SAR), Soluble Sodium Percentage (SSP), Exchangeable Sodium Percentage (ESP) and Residual Sodium Carbonate (RSC) were calculated following standard equations and found experimentally as (2.73), (27.10), (17.98) and (–22.75) respectively. Plotting the values of conductivity (EC) and sodium absorption ratio (SAR) on the US salinity diagram illustrated that most of the samples fall in the field of C3-S1, indicating high salinity and low sodium water which can be used for irrigation on almost all types of soil without danger of exchangeable sodium. Furthermore, the data indicate slight to moderate degree of restriction on the use of this treated wastewater in irrigation due to chloride hazard. RSC value was negative at all sampling sites, indicating that there is no complete precipitation of calcium and magnesium. Overall, the treated wastewater can be classified with few exceptions as suitable for irrigation use. All heavy metals analyzed were also below the permissible limit and due to these analyzed heavy metals have no any effect on the irrigation.
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Keywords: *Wastewater, Irrigation, Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), Soluble Sodium Percentage (SSP.*

I. INTRODUCTION

The world's supply of freshwater is limited and threatened by pollution from various human activities. Rising demands of water to supply agriculture, industry and cities are leading to competition over the allocation of the limited freshwater resources [1]. In both developed and developing countries, the most prevalent practice is the application of municipal wastewater (both treated and untreated) to land. In developed countries where environmental standards are applied, much of the wastewater is treated prior to use for irrigation of fodder, fiber, and seed crops and, to a limited extent, for the irrigation of orchards, vineyards, and other crops. Other important uses of wastewater include recharge of groundwater, landscaping (golf courses, freeways, playgrounds, schoolyards, and parks), industry, construction, dust control, wildlife habitat improvement and aquaculture. Thus, wastewater can be considered as both a resource and a source of different problems. Its reuse can deliver positive benefits to the farming community and municipalities. However, wastewater reuse also exacts negative effects on humans and ecological systems, which need to be identified, and assessed [2]. Wastewater contains a variety of inorganic substances from domestic and industrial sources, including a number of potentially toxic elements such as arsenic, cadmium, chromium, copper, lead, mercury, zinc, etc. Even if toxic materials are not present in concentrations likely to affect humans, they might well be at phytotoxic levels, which would limit their agricultural use. However, from the point of view of health, a very important consideration in agricultural use of wastewater, the contaminants of greatest concern are the pathogenic micro- and macro-organisms [3]. Though the actual composition of wastewater may differ from community to community, all municipal wastewater contains the following broad groupings of constituents: Organic matter, nutrients (Nitrogen, Phosphorus, and Potassium), Inorganic matter (dissolved minerals), Toxic chemicals, Pathogens and etc. Trace/Heavy metals are among the most common environmental pollutants and their occurrence in waters and sediments indicate the presence of natural or anthropogenic sources. However, the classification of US Salinity Laboratory (USSL) is used most commonly. Parameters such as EC, pH, Sodium Adsorption Ratio (SAR), adjusted SAR (adj. SAR) and the Exchangeable Sodium Percentage (ESP), Soluble Sodium Percentage (SSP) and Residual Sodium Carbonate (RSC) were assessed indicating suitability of water for irrigation purposes.

Objectives the Study

General Objective

The general objective of this study is to characterize suitability of wastewater from Bedelle Brewery Share Company for irrigation purpose.

Specific Objectives:-

- To analyze the level of major physicochemical parameters in wastewater used for irrigation purpose from Bedelle Brewery Share Company;
- To determine major heavy/trace metals in wastewater of the Bedelle Brewery Share Company.

Statements of the Problem

Industries are the major sources of pollution in all environments. Wastewater from industries includes employees' sanitary waste, process wastes from manufacturing, wash waters and relatively uncontaminated water from heating and cooling operations. High levels of pollutants in wastewater systems causes an increase in biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS), toxic metals such as Cd, Cr, Ni and Pb and faecal coliform and hence make such water unsuitable for drinking, irrigation and aquatic life[6].Many studies have indicated that the accumulation of heavy metals in the soil has an adverse effect on the growth and development of the wide variety of plant species [8]. Irrigation water that contains a certain ions at the concentration above threshold value can cause plant toxicity problem. It can results in impaired growth, reduced yield, change in morphology of plants and even its death. These heavy/trace metals when taken with plants by human can enter into human cell and cause different health impacts[9]. The problem of the industry's treatment plant also may cause the wastewater as well as the sediment to accumulate pollutants discharged from the plant. Due to this, the review will attempt to overcome the above problems which may come from improper treatment of the wastewater from Bedelle Brewery Industry.

Significances of the study

The study will be designed to conduct characterization/determination of physicochemical quality parameters of wastewater and sediment from Bedelle Brewery Share Company for irrigation purpose. The work will help to assess the pollution status of wastewater from the industry which is discharged to the nearby environment or the found community. Similarly, the study is also important for providing scientific evidences before someone uses wastewater especially for every irrigation purposes that help them to take care from being infected by poisonous chemicals and microorganisms from wastewater.

Materials and Methods

Bedelle Brewery Share Company is found in Bedelle town which is 480 km from Addis Ababa to the South west part of Ethiopia. Bedelle is found in the plain altitude at 1920N, N 08º 26` 20.9``, E 26º 18` 29.6``.

Sampling Methods and Procedure

Purposive sampling was selected for both of wastewater and soil sediment samples. Treated and untreated wastewater samples was collected in stopper fitted polyethylene bottles which was prewashed with dilute hydrochloric acid and then rinsed several times with the effluent sample before filling to the required capacity. Four sampling sites/stations was selected for wastewater collection: *Station-1* from the site before the wastewater from the whole plant get into the brewery wastewater treatment plant, *Station-2* from the site just after the treatment plant, *Station-3* just 50 m from *Station-2*, *Station-4* just 60 m from *Station-3*.

Fig.: Wastewater sample collection site

The method of sample collection at each sampling point/station was done according to the WHO Guidelines [10] for wastewater quality assessment and standard methods for the examination of waste water and the water laboratory manual [11]. The Collected samples was stored at a temperature below 4°C in an ice box containing ice freezer packs prior to laboratory for analysis.The value of pH for treated and untreated wastewater was measured by using pH meter (pH 600 Milwaukee (Mauritius) at *in-situ* and for soil sediment pH value was measured in laboratory. Electrical conductivity (EC) of wastewater sample was measured by digital conductometer. The electrical conductivity meter was first calibrated by using 0.01N KCl before analysis. Alkalinity that is total alkalinity of both samples was measured by the titration method using methyl orange indicator and titrating with standardized sulphuric acid. Calcium for both samples was measured by titration method using Murexide indicator and titrating the sample with standardized EDTA solution.Chloride was measured by titration method using Potassium chromate indicator and titrating with standardized silver nitrate solution. Turbidity was measured by digital Turbidimetrc 2100A instrument. Total Suspended Solid (TSS) and Total Dissolved Solid (TDS) were determined by gravimetric method (dried at 105°C). Magnesium was measured by titration method using Eriochrome Black T as an indicator and titrating with standardized EDTA solution.Ammonia (by stannous chloride method), nitrate, and phosphate (by phenate method) were measured by Uv-vis spectrophotometer (ELICO SL 160, INDIA). Sulphate was determined by Gravimetric Method with Ignition of Residue. Potassium and sodium were measured by Flame Emission Spectrophotometer (ELICO CL 378 Flame Photometer, India.) flame photometric method [12]. Total nitrogen was determined titrimetrically following the Kjeldahl's method (digestion, distillation and titration) as described by Jackson (1958). Total Organic carbon was determined based on the Walkley-Black chromic acid wet oxidation following $FeSO_4$ titration using either the "ferroin" indicator or potentiometrically with an expanding scale pH/mV meter method. Carbonate (CO_3^{2-}) and Bicarbonate (HCO_3^-) were determined by titration with HCl. Biological Oxygen Demand (BOD) was determined by the 5 Day BOD test while Chemical Oxygen Demand (COD) was determined in the laboratory by the standard Open Reflux Method.For trace metal analysis Flame Atomic Absorption Spectrometer (Analytikjena model nov AA 300) was used. To ensure the removal of organic impurities from the samples and prevent interferences in analysis, wastewater was digested in microwave digestion (Berghof Products + Instruments, Germany) with the combination of conc. nitric acid and hydrochloric acid. Digestion of both wastewater and soil sediment samples was according to EPA 3051 with an acid mixture using a Berghof microwave digestion system. For wastewater sample digestion 6 ml of concentrated nitric acid was added to 50 ml water sample in 250 ml beaker and the mixture was allowed to evaporate up to 15-20 ml volume of solution on hot plate. Then was allowed to cool, and 4 ml hydrochloric acid was added and was covered with watch glass and heated to near dryness up to the color of the solution become colorless; then it also allowed to cool to room temperature, then filtered and transferred to a 50 ml volumetric flask and it was filled to the mark with double distilled water [12].

II. RESULTS AND DISCUSSIONS

Concentration of heavy metals (Pb, Fe, Cu and Zn) for all sampling points was determined using Flame Atomic Absorption Spectrophotometer (Analytikjena model nov AA 300) at Jimma University and Ambo University; Applied Chemistry Laboratory. All instrumental measurements were performed using the respective hallow cathode lamps of target metals at recommended wavelengths.

Method Optimization Process

During the optimization process, different digestion procedures that employ HNO_3, HCl and H_2O_2 mixtures were selected from literature and assessed [12]. The optimization procedure was selected on the basis of clarity of digestate, minimal acid volume consumption, digestion temperature and minimum time consumed. The optimum procedure chosen based on these criteria required a total of 2 hours for the complete digestion of 50 ml of wastewater sample with 6 ml HNO_3 and 4 ml HCl. The digestion procedure gave a very clear solution which was suitable for the analysis of metals by FAAS.

III. METHOD VALIDATION PROCESS

To ensure the accuracy of Instrumental readings and to determine the reliability of the result obtained, it is necessary to perform calibration of instrument for each heavy metals selected. The Calibration curves for each selected heavy metals was setted to ensure the accuracy of the Atomic Absorption Spectrophotometer and to confirm that the result of measurements were true and reliable. Calibration curves showing absorbance versus concentration of all samples at a specified wavelength was prepared for each metal by direct analysis of the Instrument blank and three calibration metal standard solutions [13].

Table: Standard calibration points for absorbance of Cu, Zn, Fe and Pb

Metal	**Wavelength (nm)**	**Calibration Conc. (□g/mL)**	**Regression Coefficient (R^2)**	**Linear Range (□g/mL)**	**IDL(□g/mL)**
Copper	324.7	IB , 1.0, 2.0, 4.0	0.999	0 - 4	0.0010
Zink	213.9	IB, 0.5, 1.0, 1.5	0.999	0 - 1.5	0.0042
Iron	248.3	IB, 1.0, 2.0, 4.5	0.999	0 – 4.5	0.0043
Lead	217.0	IB, 2.5, 5.0, 7.5	0.999	0 - 7.5	0.0081

IB- Instrument blank

Determination Of Method Detection Limit (MDL) And Instrumental Detection Limit (IDL) Of Water Sample

The general accepted definition of MDL is the concentration that gives a signal three times the standard deviation of the blank of backgrounds signal. To determine MDL value at least seven replicate (in this particular case nine replicates were analyzed) determinations of water and blank was spiked with respective analyte and the signal was taken for each analyte by using the following equation:

MDL = SD x 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)

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, but may be used for statistical data analysis and comparing the attributes of different instruments [14]

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Table: Results of IDL and MDL for wastewater and soil sediment sample

Metal	**IDL (ppm)**	**MDL (ppm)**
Cu	0.00100	0.0162
Zn	0.0042	0.0073
Fe	0.0043	0.0828
Pb	0.0081	0.0220

Recovery Test

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 [14]. 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:-

$$R = \frac{Cs - C}{S} x\ 100$$

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: Determination of percent recovery of wastewater sample

Metal	**Cs**	**C**	**S**	**% R**
Cu (mg/L)	1.20	0.29	1.00	91±0.0115
Zn (mg/L)	1.48	0.63	1.00	85±0.0465
Iron (mg/L)	3.51	2.62	1.00	89±0.0764
Pb (mg/L)	3.51	2.51	1.00	100±0.0764

Table: Laboratory results for physicochemical parameters of wastewater

No.	Parameters	St-1	St-2	St-3	St-4
1.	pH	8.91	6.82	7.05	7.63
2.	Electrical conductivity (μS/cm at 24°C)	2003.00	1803.65	1686.82	1525.13
3.	TDS (mg/L)	1364.20	1230.00	1245.00	1164.42
4.	TSS (mg/L)	125.00	112.34	107.78	111.00
5.	BOD (mg/L)	88.60	78.93	79.00	90.80
6.	COD (mg/L)	112.75	97.54	75.76	85.95
7.	Carbonate (mg/L)	50.54	52.38	47.00	51.60
8.	Bicarbonate (mg/L)	85.51	83.85	68.60	73.60
9.	Calcium (mg/L)	290.74	258.36	153.80	148.57
10.	Magnesium (mg/L)	172.67	175.85	130.00	132.61
11.	Sodium (mg/L)	225.75	220.65	198.65	196.58
12.	Potassium (mg/L)	36.60	33.80	32.79	32.80
13.	Chloride (mg/L)	323.25	320.70	322.00	315.70
14.	Phosphate (mg/L)	42.45	34.00	33.46	19.45
15.	Ammonia (mg/L)	16.35	12.74	8.32	8.46
16.	Sulphate (mg/L)	358.00	325.54	340.00	298.58
17.	Organic Carbon (%)	13.52	13.47	10.48	5.27
18.	Copper (mg/L)	0.29	0.28	0.32	0.25
19.	Iron (mg/L)	2.62	2.60	2.58	2.60
20.	Lead (mg/L)	2.51	2.48	2.62	2.05
21.	Zink (mg/L)	0.63	0.68	0.59	0.67
22.	Sodium Adsorption Ratio(SAR) (meq/L)	2.58	2.58	2.84	2.81
23.	Exchangeable Sodium Percentage (ESP)	17.01	17.22	18.96	18.75
24.	Soluble Sodium Percentage (SSP) (meq/L)	24.15	24.62	29.91	29.72

IV. CONCLUSION AND DISCUSSION

The values of pH varied from 6.82 to 8.91 with an average value of 7.61, which indicates that the untreated wastewater from the plant is strongly alkaline and after the treatment process the nature of wastewater is slightly alkaline. The normal pH range for irrigation water is from 6.5 to 8.4. Irrigation water with a pH outside the normal range may cause a nutritional imbalance or may contain toxic ions. EC values of experimental samples varied from 1525.23 to 2003.00 μS/cm while TDS values varied from 1164.42 to 1364.20 mg/L slight to moderate degree of restriction on the use of this wastewater in irrigation due to salt build-up in soils and its adverse effects on plant growth. However, irrigation water with EC in the range of 750 – 2250 μS/cm is permissible for irrigation and widely used.Excessive sodium leads to development of an alkaline soil that can cause soil physical problems and reducing soil permeability. The water can be used for irrigation when the concentration of sodium is about 184.00 mg/L. Sodium concentrations in the samples varied from 196.58 to 225.75 mg/L (mean value = 210.40 mg/L) indicating high degree of restriction for sensitive crops on the use of this wastewater for irrigation. Sodium hazard is usually expressed in terms of Sodium Adsorption Ratio (SAR) and it can be calculated from the ratio of sodium to calcium and magnesium. SAR is an important parameter for the determination of the suitability of irrigation water because it is responsible for the sodium hazard, since it is more closely related to exchangeable sodium percentages in the soil than the simpler sodium percentage. Sodium replacing adsorbed calcium and magnesium is a hazard as it causes damage to the soil structure. It has been calculated as follows:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{+2} + Mg^{+2}}{2}}}$$

Where: Na^{+}, Ca^{2+} and Mg^{2+} are in meq/L

SAR values are varied from 2.58 to 2.84 (mean value = 2.70) and these values indicates that treated wastewater from the plant is good for irrigation.

Soluble Sodium Percentage (SSP) is also used to evaluate sodium hazard. The Soluble Sodium Percentage (SSP) was calculated by the following equation:

$$SSP = \frac{(Na^{+}) * 100}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}}$$

, where all the ions are expressed in meq/L

Water with SSP greater than 60 % may result in sodium accumulations that will cause a breakdown of the soil's physical properties. The calculated values of SSP varied from 31.38 % to 50.82 % indicating moderate degree of restriction on the use of this wastewater in irrigation. The ratio of the exchangeable Na^{+} to total exchangeable cations (Exchangeable Sodium Percentage, ESP) is a good indicator for soil structure deterioration. Although, the ESP of 10 to 15 % is generally accepted as a critical level, an ESP of 25 % may have little effect on soil structure in a sandy soil, whereas an ESP of 5 % is considered high particularly in soils containing 2:1 clay minerals like montmorillonite. The ESP of soils can be predicted quite well from the following the empirical relationship:

$$ESP = \frac{100\,(-0.0126 + 0.01475SAR}{1 + (-00126 + 0.01475SAR)}$$

The expected ESP for the experimental data would be in range of 17.01 to 18.96 which indicates medium to high degree of restriction to use for irrigation purpose. The excess sum of CO_3^{2-} and HCO_3^{-} in wastewater over the sum of Ca^{2+} and Mg^{2+} influences the unsuitability of wastewater for irrigation. In water having high concentration of CO_3^{2-} and HCO_3^{-}, there is tendency for Ca^{2+} and Mg^{2+} to precipitate as carbonates. To qualify this effect, an experimental parameter termed as RSC was used.

It can be calculated as follows:

RSC = (CO_3^{2-} + HCO_3^{-}) – (Ca^{2+} + Mg^{2+}) ----All ion concentrations are reported in meq/L

According to the USSL, RSC value less than 1.25 meq/L is safe for irrigation, a value between 1.25 and 2.5 meq/L is of permissible quality and a value more than 2.5 meq/L is unsuitable for irrigation. The calculated RSC value show that all samples have RSC less than zero and are good suitable for irrigation purposes.The most common toxicity is from chloride (Cl^{-}) in the irrigation water. Cl^{-} is not adsorbed or held back by soils, therefore it moves readily with the soil-water, is taken up by the crop, moves in the transpiration stream, and accumulates in the leaves. If the Cl^{-} concentration in the leaves exceeds the tolerance of the crop, injury symptoms develop such as leaf burn or drying of leaf tissue. The obtained Cl^{-} ion concentration of the samples varied from 315.70 to 323.25 mg/L (mean value = 320.16) representing unsuitable or tolerant plants on the use of this wastewater in irrigation.High concentration of Ca^{2+} and Mg^{2+} ions in irrigation water can increase soil pH, resulting in reducing of the availability of phosphorous. Water containing Ca^{2+} and Mg^{2+} higher than 10 meq/L (200 mg/L) cannot be used in agriculture. The results obtained shows that Ca^{2+} varied from 148.57 to 290.74 mg/L (mean value = 212.86 mg/L) and for Mg^{2+} varied from 130.00 to 175.85 mg/L (mean value = 152.78 mg/L) respectively which indicates in slight to moderate range. Another indicator that can be used to specify the Magnesium Hazard (MH) for irrigation water as in the following formula:

$$MH = \frac{Mg^{2+}}{Mg^{2+} + Ca^{2+}} * 100$$

If the value of MH is less than 50, then the water is safe and suitable for irrigation. From the calculated value, the MH values range between 737.26 – 46.85 %, (mean = 42.60 %) and the treated wastewater can be classified with few exception as suitable for irrigation use.The BOD and COD values in the present study varied from 78.93 to 90.8 mg/L (mean value = 84.33 mg/L), 75.76 to 112.75 mg/L (mean value = 93.00 mg/L) respectively. With few exceptions, the untreated and treated wastewater in this study area displayed higher values of BOD and COD. Calculated results highlight that the final effluent produced from Bedelle Brewery Share Company WWTP did not meet the Standards set by WHO.

V. RECOMMENDATIONS

- Interpretation of physical and chemical analysis revealed that the treated wastewater of Bedelle Brewery Share Company is slightly alkaline in nature which indicates high salinity of water in nature.
- Therefore it is recommended that Brewery WWTP has to be improved by correcting their treatment process. Therefore, the sustainable use of treated wastewater in agriculture can be beneficial to the environment in such a way that minimizes the side effects on the quality of downstream water resources, but it requires the control of soil salinity at the field level.
- Similarly COD, BOD and chloride values are increasing intensively which is not recommended by the WHO standards and other standard agencies which are not recommended or irrigation purpose.
- Based on these results that proper management of wastewater irrigation and periodic monitoring of quality parameters are required to ensure successful, safe and long term reuse of wastewater for irrigation. It is

recommended as a matter of high priority that treated wastewater is considered and made a reliable alternative source in water resources management.

- Agricultural wastewater reuse can effectively contribute to fill the increasing gap between water demand and water availability particularly in semi-arid areas.

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