

Physicochemical Characterization and Determination of Trace Metals in Sugar Manufactured from Sugar Cane

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Abstract The current study is interested in determination of trace metals in sugar originated from different sources such as soil, water. The analytical technique used in the study was atomic absorption spectroscopy and the results revealed that concentration of metals found in soil sample was; 51 mg/kg Fe, 6 mg/kg Mn, 2.5 mg/kg Cu, 0.36 mg/kg Cd, 8.32 mg/kg Zn, 3.92 mg/kg Cr, 5.4 mg/kg Ni, 4.08 mg/kg Co and 0.28 mg/kg Ag. Concentration of metals found in sugar sample was 0.89 mg/kg Fe, 0.28 mg/kg Mn, 0.79 mg/kg Zn, 0.88 mg/kg Cr, 0.61 mg/kg Ni, and 0.33 mg/kg Co. Concentration of copper, silver and cadmium was not detected. Concentration of metals found in effluent sample was 19.3 mg/kg Fe, 2.5 mg/kg Mn, 1.1 mg/kg Zn, 1.39 mg/kg Cr, 2.84 mg/kg Ni, 1.6 mg/kg Co and 0.05 mg/kg Cd. The physicochemical characters such as biological oxygen demand, chemical oxygen demand, temperature, electrical conductivity and pH are determined to be significant. High concentration of trace metals was determined in soil in relative to other sample and sugar sample studied is safe for consumption.

Keywords Concentration, Downstream, Effluent, Sugar, Upstream

1. Introduction

The essential metals in trace levels play vital role when present in human body. Ions of transition metals essential for life include manganese, iron, nickel, cobalt, zinc, copper and chromium. Metals are useful for metabolic activities acting as catalyst. Trace metals are micronutrients required in trace levels in plants as well as animals. Micro level imply requirement only in small concentration [1].

Although trace metals are essential to life process they pose health problem if present in concentration that exceeds the permissible level. White sugar can contain some metals impurities depending on the quality of sugar cane used in its production technology. Contents of these metals in sugar cane are a function of physical and chemical nature of the soil as well as plants which absorb these metals from

deposits on the parts of their roots by wet or dry deposition from polluted environment [2, 3].

Trace heavy metals like Ag and Cd can exist in association with macronutrients. This association can influence the proper work of the metals by pairing. The main source of toxicity now a day is food. Food processing methods are commonly responsible for the contamination of human food by toxic metals.

The maximum permissible level of toxic metals in human food has been established by the FAO/WHO expert committee on food additives recommended a provisional maximum tolerable daily intake for Cd, Co, Ni, Cu and Zn from all sources of food, air, water 1-2, 3.5-4, 2-4, 2-2.5 and 8-15 µg/kg of body mass respectively [4, 5, 6].

Sugar factory is one of the biggest factory manufacturing sugars for consumption of mankind. The factory uses fertilizers to produce sugar cane and chemicals to process cane juice. Hence at different stages of sugar processes there are chemicals in use that can contribute metal ions directly or indirectly to the sugar products. Therefore this study become prominent in exploring the level of metal ions and forwards the expected outcome.

The objective of the work is

- To determine the concentration of trace metals in sugar sample.
- To characterize effluents and river in terms of BOD, COD, pH, temperature, electrical conductivity and TDS.

The significance of the study is to add the information about the relationship between soil, river and effluents in accommodating metal ions.

2. Materials and Methods

2.1. Instrumentation

ELICO SL-194 India atomic absorption spectrophotometer (AAS), Hana pH meter (H18314 Japan), portable conductometry (handy play HF Japan), 101-0 Electric Heated Blast Dry Box Oven and SX-10 Box Resistance Furnace Controller Box and TDS meter.

2.2. Chemicals and Reagent

Uni. Chem. Chemical reagents N29508-4K Con. HNO₃ (assay 65-68%) UN 1789 IATA 37%HCl, H44 H47055-45 30% H₂O₂, 2ml olive oil and stock solution of metal ions under study.

2.3. Methodology

2.3.1. Soil Sampling

Soil sample was collected from cultivated soil where sugar cane is planted and samples are collected from different points separated at some distance from each other. At each place soil sample has been taken at an average depth of 15cm and totally 1kg obtained from each point of collection. During collection soil sample was packed into aluminum foil of thickness 0.08mm and preserved in ice bag until analysis [7, 8].

2.3.2. Sugar Sampling

Sugar samples were collected two times from the factory product and the total of 1kg sugar sample was collected in each cases. The first sample was taken from the products manufactured within the first 15 days of the month whereas the second case was collected from the products manufactured within the second 15 days of the month [8]. Different packages of the product were used during collection.

2.3.3. Effluent Sampling

Effluents were assigned to be collected from two positions with respect to sugar factory. The first position is at outlet (E1) and the second is at the point where effluent mix with river (E2). During collection polyethylene bottle was used which was rinsed with HNO₃. After collection the sample was stored in refrigerator before any determination has been taken place. Temperature, electrical conductivity, total dissolved solid, pH, biological oxygen demand and chemical oxygen demand of the sample were determined before metal analysis has been performed [9].

2.3.4. Water Sampling

There were two positions of sample consideration when water sample collected. The first position is the river before effluent mixed and named to be upstream. The other option is the river part after effluent is added which was assigned to be downstream [10]. The apparatus used to collect sample is polyethylene which was rinsed with HNO₃.

2.4. Sample Preparation

2.4.1. Soil Sample Preparation

The soil collected was placed in the oven at 85⁰C to be dried and then powdered to uniform particle size with mortar and pestle. The total soil sample taken for analysis was 2.5g and this amount was dissolved in distilled water. The solution was mixed with mixture of 3ml of 0.02N HNO₃ and

H₂O₂ and placed on hot plate for 25minutes at 35⁰C [11].

2.4.2. Sugar Sample Preparation

The sugar sample was finely powdered with mortar and pestle in platinum dish. 7.5g of the finely powdered sugar sample was placed in crucible. The crucible with sugar sample was placed in oven at 105⁰C for about 20hours. After the sugar sample dried it was further placed in muffle furnace and ashed at 500⁰C. The white ash formed was rinsed with deionized water and covered with watch glass and put on hot plate at 35⁰C without boiling and added 3ml of 0.02N HNO₃. The sample was cooled for some time and reheated on hot plate. The watch glass has been opened to allow excess HNO₃ to escape. Additional 5ml of HNO₃ was added until digestion complete. The sample was heated after further cooling and the mixture of water and HCl in the ratio of 50:50 was added and reheated [12].

2.4.3. Effluent Sample Preparation

The effluent sample was taken into 250ml beaker and added 3ml of 0.02N HNO₃ and covered with watch glass to heat gently on hot plate at 35⁰C without boiling. The sample was cooled and another 3ml of HNO₃ was added and placed on hot plate and reheated at 35⁰C. Repeatedly cooling and heating has been taken place until digestion completes [13].

2.4.4. Water Sample Preparation

The water sample was filtered with what man filter paper No 42. 100ml of the filtrate was measured and added into 250ml beaker. Into the beaker 3ml of HNO₃ was added and placed on hot plate at 35⁰C. The beaker was covered with watch glass and heated gently. The watch glass was removed to avoid excess HNO₃. After some time the mixture of HCl and HClO₄ was added to dissolve any precipitate in the sample and lastly the sample was filtered [14].

2.5. Determination of BOD

The effluent sample was neutralized to pH 7.2 by adding 3ml of 0.1N NaOH. For BOD measurement two half filled 300ml bottle with dilution water were prepared. One of the bottles for each sample dilution and the one with dilution water was incubated for five days at 20⁰C±1. DO determination was applied before incubation and after incubation. After five days the remaining DO was measured [15].

$$= \frac{\frac{mg}{L}, BOD5}{\text{Percentage of sample added into incubator}} \times 100$$

$$= \frac{\text{initial DO of diluted sample} - \text{DO of sample after five days}}{\text{Percentage of sample added into incubator}} \times 100$$

2.6. Determination of COD

For the determination of COD 45ml of the sample was taken into 250ml volumetric flask and 1.5ml of potassium dichromate was added in the flask. The mixture was refluxed for 6hours, cooled and excess dichromate solution was

titrated with 0.1N Mohr salt. The remaining excess dichromate revealed the consumed amount of COD [16].

2.7. Determination of pH

The electrode was calibrated with buffer solution at pH of 4 and 9. The calibrated electrode was rinsed with deionized water and wiped with a tissue paper; finally the electrode was immersed in sample solution of unknown pH.

2.8. Metal Analysis

Metals were determined typically by flame atomic absorption spectrophotometer. Atomic absorption spectrophotometer (FAAS) analyses are utilized for the determination of Ag, Cd, Co, Cr, Cu, Fe, Mn, Ni and Zn.

Calibration curve was established using standard solution of each metal ion. The stock solution of the metal ion was prepared in 0.02N HNO₃. 1000mg/L of each metal ion was prepared by weighing 1g of each metal ion and dissolve in water and further mixed with HNO₃ prepared from 2ml of 68% assay dissolved in 100ml distilled water. Working solution was prepared by measuring 1ml of stock solution in

order to prepare range of concentration [17].

3. Results and Discussion

Method validation: to validate the analytical performance of the instrumental analysis the determination of instrument and method detection limit, the analysis of initial and continuing calibration standards, Laboratory Fortified Blank (LFB) and LFB duplicate Analysis, and Laboratory Fortified Matrix (LFM) and LFM duplicate Analysis were done for each analyte.

From table 3 the pH of cane wash, mill house, boiling house, upstream and downstream was 7.15, 6, 6.06, 6.93 and 6.92 respectively. The results indicated that the pH of cane wash, upstream and downstream samples was nearly neutral. Millhouse and boiling house were slightly acidic. The upstream and downstream water samples exhibited similar pH value. The acidity of effluents such as mill house and boiling is because of the fact that sucrose decompose into monosaccharide, organic acids and alcohols [17].

Table 1. Instrument optimized condition for specific metals

Metal	Ag	Cd	Ni	Mn	Co	Zn	Fe	Cr	Cu
Wavelength(nm)	328.1	228.8	232	279.8	240.7	213.9	248.3	357.9	324.7
Slit width(nm)	1	1.5	2.5	2.5	2.5	1.5	2.5	0.75	1
Current(Ma)	04.4	05.4	06.6	05.5	07	06.4	06.4	05	06.4

Table 2. Regression equations, correlation coefficients and detection limits

	Regression	R2	IDL(mg/l)	Spike level(mg/l)	MDL(mg/l)	10*MDL	Recovery	RSD
Mn	1.01X+0.21	0.998	0.05	0.23	0.3	3	89.91	1.02
Cr	3.1X+2	0.981	0.001	0.12	0.41	4.1	79.1	5.6
Cu	2.01X+2	0.992	0.001	0.45	0.01	0.1	78.5	7.08
Ni	0.01X+2	0.978	0.005	0.32	0.02	0.2	98.1	2.04
Fe	3.5X+2	0.985	0.001	0.15	0.5	5	85.6	5.6
Co	1.02X+2	0.958	0.001	0.6	0.46	4.6	87.4	4.5
Cd	4.01X+2	0.987	0.002	0.12	0.8	8	96.5	3.3
Ag	0.06X+2	0.968	0.002	0.54	0.9	9	84.5	1.04
Zn	1.3X+2	0.987	0.003	0.9	0.06	0.6	93.5	2.2

Table 3. Physico chemical characteristics of effluent and water sample

Effluent type	pH	Electrical conductivity	T(°C)	TDS	BOD	COD
Cane wash	7.15±0.0057	0.16±0.014	30±1	105±1	40±1	105±2.5
Mill house	6±1	0.395±0.007	40±1	220±1	1596±11	4600±100
Boiling house	6.06±0.5	0.6±0.1	42±1	360±10	1506±11	16789±105
Up stream	6.93±0.01	0.07±0.01	22±1	49±0.1	50±1	44±0.1
Down stream	6.92±0.01	0.09±0.1	26±1	50±0.1	59±1	56±0.04

Table 4. Concentration of trace metals in different samples of sugar effluent, water and soil

Metals	E1	E2	Upstream	Down stream	Soil	Sugar	WHO
Cu	ND	ND	0.08±0.01	0.14±0.01	2.8±0.26	ND	0.1
Cd	0.5±0.25	0.42±0.03	0.24±0.02	0.14±0.01	0.36±0.03	ND	0.007
Zn	1.12±0.41	0.3±0.01	0.3±0.045	0.46±0.01	8.55±0.2	0.81±0.03	0.5
Cr	1.35±0.05	1.09±0.1	0.43±0.03	1.14±0.05	3.95±0.04	0.8±0.072	0.05
Ni	2.75±0.46	2.64±0.08	1.6±0.1	1.75±0.13	5.4±0.1	0.64±0.026	0.01
Fe	20.61±1.67	16.25±0.35	10.72±0.23	18.2±0.72	51±6.55	0.9±0.07	0.3
Mn	2.5±0.42	2.3±0.01	0.67±0.046	1.3±0.09	0.75±0.12	0.293±0.06	0.05
Co	1.65±0.2	0.453±0.045	0.416±0.03	1.2±0.1	4.12±0.15	0.33±0.01	0.3
Ag	ND	ND	ND	ND	0.31±0.04	ND	-

ND-not detected, E1-effluent without water, E2-effluent and water

Total dissolved solid (TDS): it increases with increasing temperature since most solids dissolve faster as temperature increase. Cationic species favors acidic media and hence amount of dissolved mater increase in the millhouse and boiling house [17].

Electrical conductivity (EC): the electrical conductivity was determined to be 0.09-0.15mS/cm. the conductivity is directly related o the dissolved solutes and ions. The results indicated that effluents in process revealed more electrical conductivity than the other cases. It is because chemical processes emerged and taken place so as to release more ions and soluble solutes [18].

Temperature: according to the study in table 3 cane wash effluent temperature is less than millhouse and boiling house. The step where exchange of heat energy and occurrence of chemical reactions such as decomposition expected to take place in millhouse and boiling house [18]. The temperature of water sample obtained from the river determined to be lower than any of the sample analyzed.

Biological oxygen demand (BOD) and Chemical oxygen demand (COD): of millhouse and boiling house determined to be higher compared to the other samples. BOD is biologically active species available during the process; therefore it indicates that microorganisms activating decomposition reaction were more than the other three samples. COD is oxygen demanding chemicals for oxidation; hence there are different organic compounds require oxygen for further oxidation processes. In upstream, downstream and cane wash the value of BOD and COD was determined to be lower since no significant chemical processes involving decomposition taken place [16].

The concentration of copper in E1, E2 and sugar sample was not detected and indicated as not detected. The concentration of silver is also not detected in all the cases and only significant to be detected in soil sample. The concentration of cadmium is negligible in sugar sample and not detected. In the other metal ions significant amount is detected and compared among samples.

The concentration of metal ions determined in downstream was greater than that of upstream. This was explained in terms of the fact that the river was exposed to further metal ions in effluent released from the factory

processing stages during sugar manufacturing [17]. The concentration of some of the metal ions varied among effluent at the factory (E1) and effluent at the gate to the river (E2). According to the comparison the concentration of Cd, Zn, Cr, Ni, Fe, Mn and Co in E1 was greater than in case of E2. It was because concentration expressed as amount per diluting solvent; as the effluent move longer and longer along the river; the amount of metal ions added to more water. Except in case of cadmium the concentration of metal ion in soil exceeded the concentration in the other sample [16]. The concentration of all the metals determined in sugar is less than any of sample analyzed; since sugar is the final product passed through different refining and purification stages [18]. Thus soil contributes more of the metal ions to sugar from plantation to production stage through direct or indirect influence.

The concentration of Cd, Cr, Ni, Fe and Mn in sugar effluents exceeded the concentration established according to EPA.

4. Conclusions

Sugar is the product obtained from sugar cane after several factory processes have been taken place. These different stages use additives at several steps for production, purification, extraction and bleaching. At each of the stages there are main products and byproducts. The BOD, COD and TDS of millhouse and boiling house effluent was determined to be greater than the three cases cane wash, upstream and downstream. According to the current study the source of metal ions in sugar was determined to be from the soil and rarely from irrigation. The concentration of some metals was determined to be greater than EPA standards established for industry effluents. The concentration in sugar sample was almost safe in relative to world health organization.

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