Characterisation and Quantification of Bioprocessing Effluents from Coffee, Dairy and Tannery Plants

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Abstract - There is an increasing rate of environmental pollution resulting from high emission rates from bioprocessing industries in Kenya. This study provides information on the characterization of bioprocessing effluents collected from the dairy, coffee, and tannery industries in Kenya. To achieve this, 20-litres containers were used to collect samples of effluents from the 3 industries and then transported using plastic containers to JKUAT chemistry laboratories within 24 hours for analysis. Each sample was divided into 3 different 500 ml bottles, and the experiment was replicated 3 times to minimise analytical errors. The pollutant levels noticed at the different industries were notably high in tannery and least in the dairy effluents. The study also found that tannery effluents had the highest concentrations of various cations, followed by coffee effluents. Dairy effluents showed the lowest quantities of cations when compared to tannery and coffee effluents. The concentrations of CO_3^{2-} were the highest in tannery effluents (286 mg/l), while those in dairy were the least (28 mg/l). Based on the results obtained, there is need to treat the bioprocessing effluents before discharge to the water body.

Keywords: Bioprocessing effluents, BOD_5, COD, Cations, EC TDS, and TSS

I. INTRODUCTION

There is an increasing rate of environmental pollution resulting from high levels of heavy pollution loads because of the presence of harmful compounds and poisonous metallic compounds emitted from bioprocessing industries [1], [2]. These effluents have got high environmental pollution compared to other sources and, as a result, harm the typical existence of the recipient water bodies and the adjacent dry land [3]. These industries emit gases and other dissolved components, which affect agricultural activities and, at the same time, lead to increased greenhouse gas emissions, hence, global warming. Different wastewaters have different levels of nutrient compounds that are neutralized by growing algae [4].

Dairy bioprocessing effluents is characterised by powerful colour, irritating odour, excess BOD of about 47,500 mg/L, and COD of up to 94,000 mg/L [1] and the pH that varies [5]. Physical and chemical techniques are regularly utilized in dairy wastewater treatment; however, these strategies are extravagant and therefore, there is need to treat dairy bioprocessing effluents [6]. Dairy industry wastewater displays a muddled framework comprising of various parts, including poisons from handled crude materials, synthetics, and deposits of innovative added substances utilized in individual tasks. About the food industry wastewater, treatment measures need to guarantee first of all necessary nature of effluent emitted [7].

Tannery discharges are always portrayed by their high dissolved solids, high pH, reddish dull brown colour, and high BOD. The other significant chemical composition from tannery discharge are chromium and sulphide compounds [8]. Mixing these organic compounds with water and then releasing them to the water bodies not only pollutes the waters but also makes it unsuitable for drinking general utilization and irrigation purposes.

When dumped into the water bodies, wastewater from the coffee industry consumes the oxygen available, leading to the demise of aquatic life due to extreme levels of acidity and inadequacy of oxygen [9]. This can lead to water inadequacy for domestic and industrial use, including the processing of bio-products in industries. Water contamination is brought about by natural, inorganic, organic, radiological, or actual substances in the water that corrupt its quality. The presence of poisonous and undesirable substances and microbes past specific cut off points likewise cause water contamination [10].

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The contamination of water bodies because of the release of low quality effluents represents a genuine danger to individuals and oceanic living organisms since they depend on water for food and survival. The issue is more serious in third world nations where high growth rate and industrialisation has expanded the intricacy of effluents. Lately, scientists have focused on the conceivable reuse and reusing of different effluents where dairy ventures are no exemption. Nonetheless, when these effluents are not treated and are just discharged into streams, they add to eutrophication by the incorporation of nitrogen and phosphorus compounds [11]

The bioprocessing effluents should be effectively treated of requires a decent information on the amount, quality, and variations in the discharge components. In this way, in recognizing wastewater, physicochemical properties are very vital to characterize the qualities of the treatment interaction. Also, information on some physicochemical boundaries gives a fundamental evaluation of the quality and the level of water contamination. [12]. Therefore, this study aims to characterize and quantify the chemical composition of effluents from three bioprocessing industries.

II. MATERIALS AND METHODS

A. Sample Acquisition and Preparation

In this study, bioprocessing effluents were collected from three (3) industries, namely, New Kenya Cooperative Creameries, Leather Industry of Kenya, and Sasini coffee factories. Before collection, the effluents were first stirred thoroughly to mix any present sediments, and then the mix was kept in 20-litre containers, labelled and preserved. The samples were then filtered through Whiteman 41 filter paper with diameter of 125 mm for the elimination of large materials and taken to the laboratory for analysis.

B. Characteristics of Bioprocessing Effluents

The three 20-litre samples were placed into seven different 500ml sampling bottles for every bioprocessing effluent and taken to a laboratory where they were further divided into three different portions for each sample and were subjected to various tests among them, total dissolved solids (TDS), biological oxygen demand in 5 days at 20°C (BOD$_5$), pH, total solids (TS), total suspended solids (TSS), chemical oxygen demand (COD) and electrical conductivity (EC). Effluent temperature (°C) and colour were recorded using a thermometer [13] and a Pt-Co colour unit, respectively, while EC and pH and values were estimated using a computerized multi-range conductivity meter (Model

Hanna HI 9033, Singapore) and portable digital pH meter [14] respectively. The levels of TS, TSS and TDS, were determined gravimetrically following standard methods [15]. Similarly, dissolved oxygen (DO), BOD$_5$, COD were determined based on standard methods [16]. Concentrations of CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and NO_3^- in the effluents were estimated by AAS [17] through the mixing of the samples in ascorbic acid and concentrated sulphuric acid mixer [15]. The tests were replicated to reduce analytical error that may arise as much as possible. The outcomes were contrasted with effluent values for NEMA limits for discharge effluents to the environment.The detailed procedures for the determination of the aforementioned parameters are outlined in the following sections.

a) Biological Oxygen Demand

To determine the BOD of the effluents, 40 ml of the effluent was diluted with 2 ml of magnesium sulphate 5 ml of phosphate buffer, 1 ml of ferric chloride, and 1ml of calcium chloride. The initial DO of the diluted mixture was recorded, then the samples were transferred to BOD bottles for incubation at 32°C for 5 days. The value of BOD$_5$ after incubation for 5 days which corresponds to the final DO was recorded. BOD was calculated using equation (1), in which D_1 is DO of the sample immediately after preparation (mg/L), D_2 is DO of the sample after incubation for 5 days, and P is a decimal volumetric fraction of the sample used.

$$BOD \ (\frac{mg}{L}) = \frac{D_1 - D_2}{P} \qquad (1)$$

b) Chemical Oxygen Demand

The reflux method was used to analyse the COD levels in the effluents where 1.5 ml of potassium dichromate ($K_2Cr_2O_7$) and 3.5 ml of H_2SO_4 were mixed to form the reagent. For each type of effluent, -three (3) samples, each measuring 2 ml was placed in test tubes in which 1.5 ml of the reagent was added. Thereafter3.5ml of sulphuric acid was added cautiously down within of the vessel for the formation of an acid layer under the sample. Each test tube containing the samples was firmly covered and each test tube was inverted several times to ensure thorough mixing [18]. The tubes were then placed inside a water bath preheated to 150°C and refluxed for 2 hours behind a protective shield. Thereafter, 0.10 ml (1-2drops) of ferroin indicator was added to the samples while stirring rapidly. The samples were then titrated with standardized 0.10M (Ferrous Ammonium Sulphate) FAS. As control/blank, 50 ml of distilled water containing the bioprocessing effluents was refluxed and titrated. COD was computed using

equation (2), in which A is the volume of FAS used for blank, B is the volume of FAS used for sample M=molarity of FAS and 8 is milliequivalent weight of oxygen.

$$COD = \frac{((A-B) \times N \times 100 \times 8)}{Volume\ of\ sample} \quad (2)$$

c) Colour Measurement

Colour measurement for the different effluents was estimated by the use of a hunter lab colour contrast meter (Minolta, Chroma Metre CR-200; Minolta Camera Co., Ltd., Osaka, Japan). White balance was done before specimen estimation of colour with the help of a black and white ceramic plate. Colour estimates were replicated to reduce analytical error. The values for L*, a*, and b* were documented for each specimen by taking a colour reading in three (3) sections of the specimen. A calorimeter head was set straightforwardly on the outer layer of each example and the readings taken. The procedure was repeated six (6) times, and the average computed.

Qualities displayed on the concealing meter screen as L* for delicacy/obscurity, a* for chromaticity from red (+) to green (-) hub, and b* for chromaticity from yellow (+) to blue pivot (-) were used for registering the Hue p point as Hue angle= [tan - 1(b*/a*)] [19]. Chroma (C*), which is a pointer for immersion of shading and is comparing to, not set in stone utilizing condition (3).

$$C^* = [a^{*2} + b^{*2}]^{1/2} \quad (3)$$

Total colour difference (ΔE*) of the samples was calculated as shown in equation (4). In the equation, Δb* is the blue/ yellow difference and Δa* is the green/ red difference.

$$\Delta E* = \sqrt{\Delta a*^2 + \Delta b*^2 + \Delta L*^2} \quad (4)$$

d) Determining Cations in the Effluents

To determine the phosphates (PO_4^{3-}) concentration in the effluents, 3.5 ml of ammonium molybdate solution and 2.5 ml of ascorbic acid were added to a sample of the effluent while swirling. The mixture was then diluted with 50 ml deionized water and allowed to stand for maximum colour development. It was then placed in a spectrophotometer and the absorbance read. On the other hand, the concentration of nitrates (NO_3^-) in the effluents was determined as follows. To a sample of effluent, - ml of sulphuric acid was added and mixed while swirling, then allowed to come to thermal equilibrium in a cold-water bath (0-10ºC). Brocine-sulfanilic acid was added to the mixture and diluted with deionized water, then placed on a 100ºC hot water bath for maximum colour development. It was then placed in a spectrophotometer and the absorbance read.

To determine the concentration of carbonates (CO_3^{2-}) in the effluent, a 0.02N sulphuric acid was prepared and then mixed with 50 ml of each sample in a round bottommed flask. Three (3) droplets of bromocresol green were added to the solution, and this was titrated against the prepared acid until the solution turned yellowish. This procedure was replicated for every sample while recording the figures obtained. The concentration of carbonates (C) present in the effluent was calculated using equation (5). In the equation, N is the normality of acid and A is the volume of acid.

$$C = \frac{(A) x N x 50000}{V} \quad (5)$$

To determine the concentration of sulphates (SO_4^{2-}) in the samples, Ammonium molybdate solution and ascorbic acid were added to a sample of the effluent containing sulphate compounds while swirling. A 2 ml of buffer was then added, followed by a spatula full of barium chloride. The mixture was allowed to stand for maximum colour to develop. It was then placed in a spectrophotometer and the absorbance read.

III. RESULTS AND DISCUSSION

The results for physico-chemical characteristics of bioprocessing effluents from the 3 industries are summarised in Table 1 together with allowable limits for discharge by the National Environmental Management Authority (NEMA) of Kenya. These results are discussed in detail in Sections 3.1 to 3.4.

Table 1 Physico-chemical characteristics of bioprocessing effluents from three industries

Parameters	Dairy	Coffee	Tannery	NEMA Limits
Temperature (°C)	27±1	28±0.5	24±1.2	20-35
pH	4.6±0.2	2.6±0.2	10.5±0.5	6.0-9.0
EC (mS/cm)	265±1	668±1.2	398±1.0	-
TSS (mg/L)	420±1	510±2	1200±6	-
TDS (mg/L)	123±05	328±7	188±10	2000
COD (mg/L)	118±5	176±1	128±0.5	1000
BOD_5 (mg/L)	1200±11	800±10	700±7	500
DO	1.24±0.4	0.81±0.1	5.20±0.2	-
CO_3^{2-} (mg/L)	28±0.3	80±0.8	287±0.5	-
SO_4^{2-} (mg/L)	40.80±0.4	52.76±0.1	49.51±0.5	-
PO_4^{3-} (mg/L)	0.37±0.04	0.11±0.01	0.38±0.06	30
NO_3^{-} (mg/L)	0.49±0.02	3.50±0.04	7.20±0.01	100

A. Temperature, PH and Colour

The results in Table 1 show that the minimum temperature of the effluents varied from 24±0.1 to 28±0.1°C. The highest temperature (28±0.5 °C) corresponded to the coffee effluent, while the least (24±1.2 °C) to the tannery effluents. The mean temperature for the dairy industry effluent was 27±1°C, and this value was well below the permissible limits by NEMA. Different examination reports show that bioprocessing discharge temperatures relies upon the industrial production process, and its standard reach is 22 to 40 °C [20], [21], and [22].

It was also observed that the pH values for the different effluents ranged from 2.6±0.2 to 10.5±0.5. The effluents from coffee industries had the least pH (2.6±0.2), which was well below the recommended standard cut off points. The highest mean value (10.5±0.5) was found in effluents from the tannery industry due to the extreme utilization of sodium sulphide and calcium oxide in the creation of the lime streak. The pH value for the dairy industry was found to be 4.6±0.2, which was well underneath the recommended standard cut-off points.

In regards to colour, it was noted that this parameter was different for effluents from the different bioprocessing industries. The colour range for the effluents was between 49.24±0.5 and 68.48± 0.9 Pt-Co units. Effluents from the coffee industry had the highest value of 68.48± 0.9 Pt-Co units, followed by tannery with 61.92± 0.1 Pt-Co units, and dairy came last with 49.24±0.5 Pt-Co units (Fig. 1).
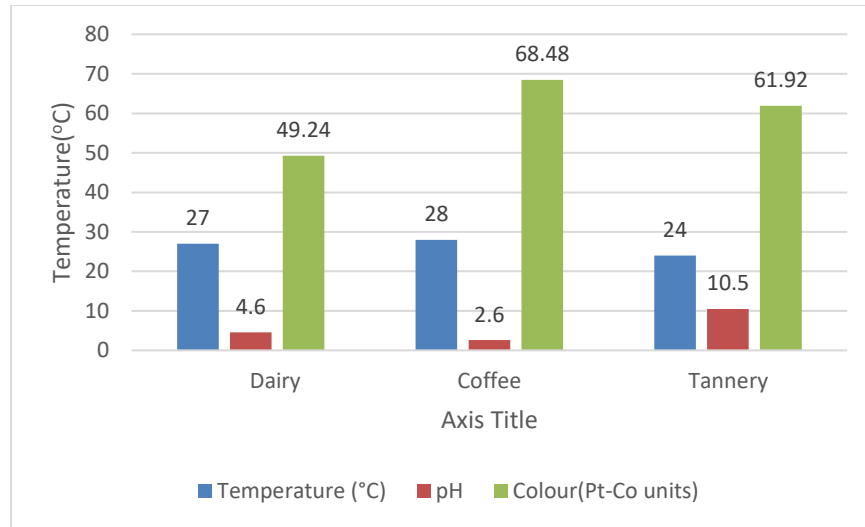
Fig. 1: Variation of temperature, pH, and colour of effluent for different bioprocessing industries.

B. EC, TDS, TSS, and TS

The average electrical conductivity (EC) values for the effluents varied from 265 ± 5 to 665 ± 10 mS/cm, the highest being 665 ± 10 mS/cm which corresponded to the coffee industry. The values for the tannery and dairy were 75 ± 1 and 265 ± 5 mS/cm, respectively. The high EC values obtained are indicators of the existence of large amounts of salts in the discharges [16]. As for TDS, the mean concentration values ranged from 123 ± 3 to 328 ± 1 mg/L. The largest value of 328 ± 1 mg/L corresponded to the coffee effluent while the least value of 123 ± 3mg/L to the dairy effluents while tannery effluents had a mean TDS of 188 ± 10 mg/L. The values of TDS acquired were lower than the accepted discharge limits of 2000 mg/L, which is a recommended threshold for releasing discharges into water bodies. The span of the total suspended solids (TSS) was from 420 ± 9 to 1200 ± 1 mg/L. The tannery effluent had the highest mean value of 1200 ± 1 mg/L and this was followed by coffee (810 ± 5 mg/L) and dairy (420 ± 9 mg/L) effluents. As observed with the other parameter, the tannery effluent had the highest value mean value of 280 ± 3mg/L, and this was followed by coffee (230 ± 6 mg/L) and dairy (200 ± 1 mg/L) effluents (Fig. 2).
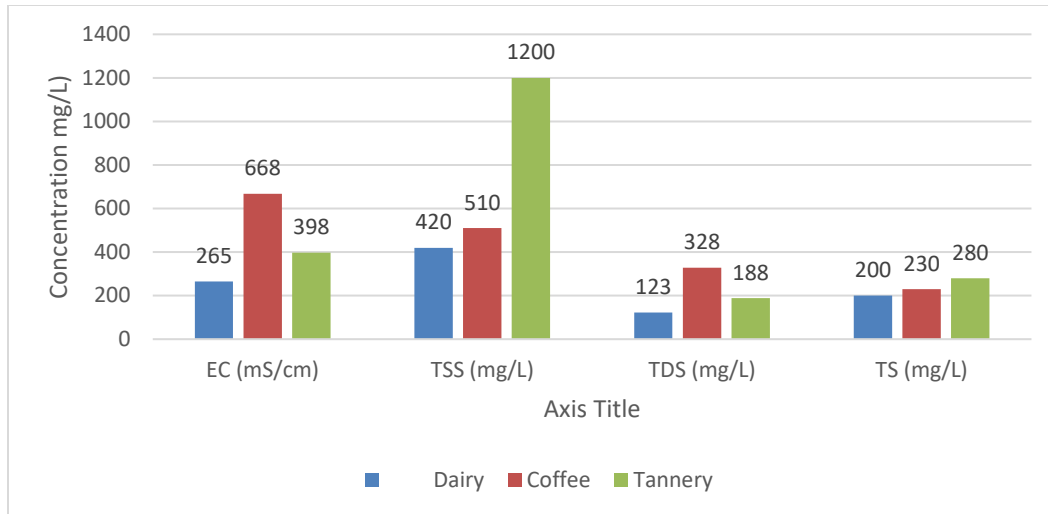
Fig. 2: Variation of TSS, TDS, and TS concentration for different bioprocessing industries.

C. DO, COD and BOD5

The average values of COD and BOD_5 were 118 ± 5 to 176 ± 1 mg/L and 700 ± 6 to 1200 ± 2 mg/L, respectively. The highest value (1200 ± 2, 176 ± 1), belonged to the dairy effluent as this has high organic content represented mainly by carbohydrates and proteins present. All the BOD_5 values are higher than the permissible values for discharge to surface water bodies.

Discharges from industries to water bodies affect the water by intensifying the colouration, increasing the BOD_5, pH and COD. The findings from this study indicates that the average values of DO in dairy, coffee, and tannery discharges were 1.24 ± 0.01, 0.81 ± 0.02, and 5.20 ± 0.2 mg/L, respectively. The DO concentration in the range of 5.0-8.0 mg/L is favourable for maritime life, and DOES under 4 mg/L is dangerous [23] and [24]. According to [25], the minimum levels of DO (≤4 mg/L) present in the discharges were because of excessive natural contamination, showing an undeniable degree of BOD5 in the effluents (Fig. 3).
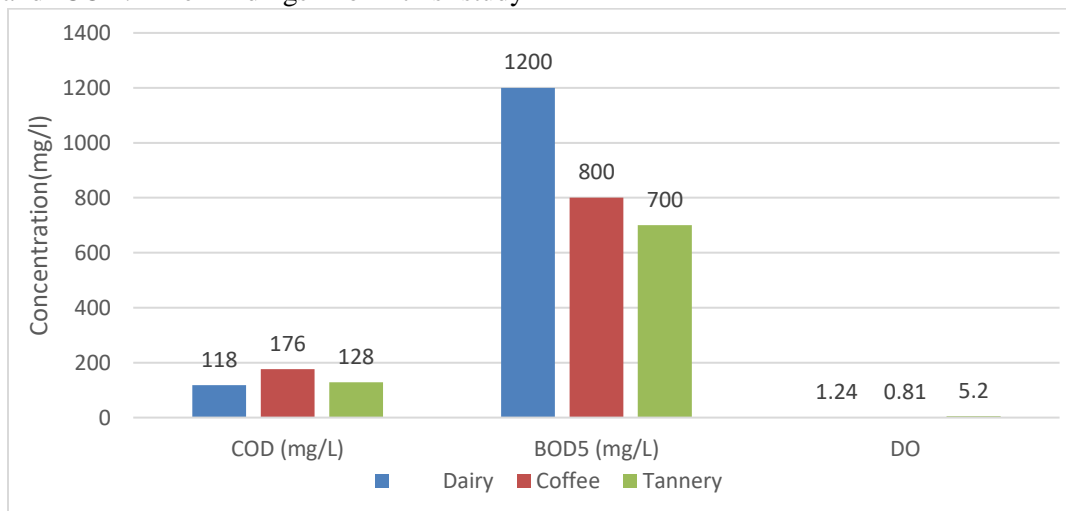

Fig. 3 Variation of COD, BOD5, and DO concentration for different bioprocessing industries.

D. CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and NO_3^{-}

three companies ranged from 280.5 to 286.9 mg/L on average (Fig. 4). Tannery effluents had the highest value of (286.9 mg/L), whereas dairy effluents had the lowest value of 28.5mg/L. The concentration of coffee effluents was 80.8 mg/L. The CO_3^{2-} values obtained in all the effluents were within the allowed limits, making them eligible for release into the water body.

The average SO_4^{2-} concentrations of effluents from the three industries ranged from 40.80 to 52.760 mg/L, as shown in Fig. 4. Coffee effluents had the highest value (52.76 mg/L), whereas dairy effluents had the lowest value (40.80). The concentration of tannery effluents was 49.51mg/L. The SO_4^{2-} levels found in all effluents were lower than the recommended levels and therefore safe for release into the water body.

The mean PO_4^{3-} concentrations of effluents from tanneries portrayed the highest value of 0.380 mg/L,

The CO_3^{2-} concentrations in the effluents from the ensued by the dairy industry with 0.370 mg/L, as shown in Fig 4. The coffee industry's effluents registered the lowest concentration of 0.110 mg/L. The PO_4^{3-} values estimated in different wastewater specimens were lower than the permissible values, indicating that the effluent samples were eligible for further investigation. All of the effluents had PO_4^{3-} concentrations that were lower than the required limits, making them safe for discharge into the surface of the water.

The values of NO_3^{-} in effluents from various industries were 0.49 ±0.01 to 7.20±0.02 mg/L. Tannery effluents had the highest concentration (7.20±0.02), whereas dairy effluents had the lowest concentration (0.49±0.01) and that of coffee effluents was 3.50±0.04. All the NO_3^{-} values attained were below the allowed limits and therefore eligible for discharge into the water body.
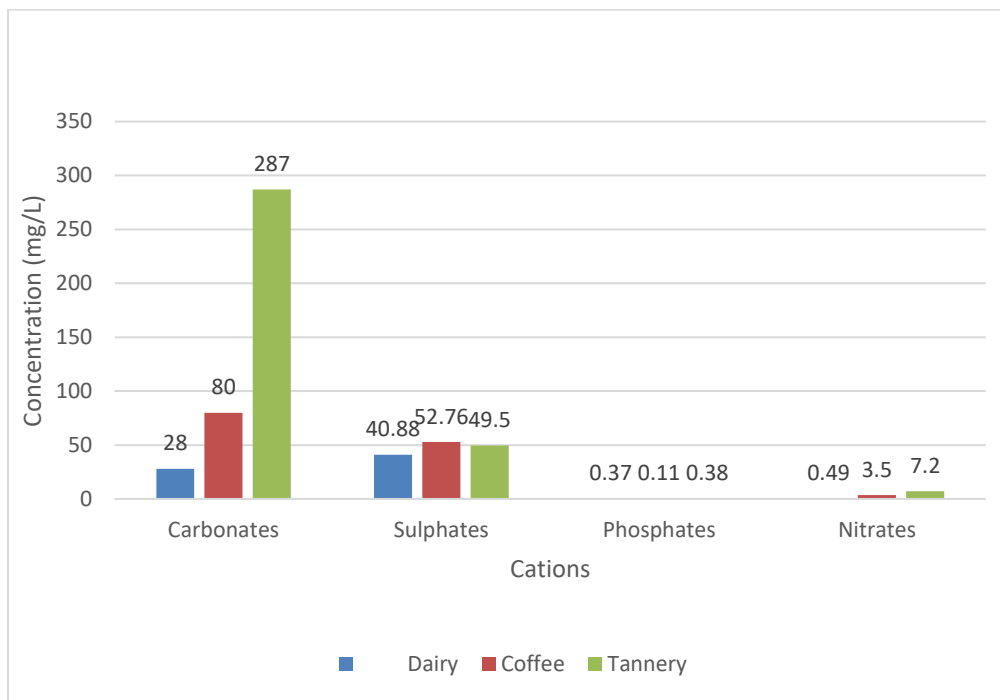

Fig. 4. Variation of cations concentration for different bioprocessing industries.

IV. CONCLUSIONS

The values of the characteristic parameters of the bioprocessing effluents vary widely and are influenced by the chemical components and the raw materials of the products used as well as the processing steps involved. The findings indicated clearly the important physico-chemical specifications of all the discharges from the three industries studied exceeded slightly the standard permissible NEMA limits for discharges. Due to growing environmental concerns and limited worldwide freshwater supply, clean technologies and water reuse, and advanced treatment systems are being developed and adopted to avoid water

contamination and to meet requirements before the discharge of this effluent to surface water bodies. Therefore in this regard, serious measures should be adopted to scrutinize the standards of the bioprocessing effluents intermittently and put in place their fundamental remedies so that toxic substances do not get access to the surrounding environment. It is important to carry out more analysis using advanced technologies to improve on investigation and quantification of the possible contamination sources

AUTHOR CONTRIBUTIONS

J. O. (MSc. student) was in charge of conceptualization, conducted formal analysis, data interpretations, and wrote the original manuscript.
C.L (Professor), B.G. (Ph.D.), S.O. (Doctor) guided the experiment in the whole process. Was in charge of experiment guidance and paper revision.

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