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## **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 from 3 industries in Kenya. To achieve this, samples of effluents were collected 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. Physico-chemical parameters such as 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) of collected samples were analysed. The mean concentration levels were found to be (118±5, 176±10, and 128±3) for COD and (1200±2, 800±1 and 700±6) for BOD 5 for dairy, coffee, and tannery effluents, respectively. These values were found to be slightly higher than the standard removal levels. The pollutant levels noticed at the different industries were notably high in tannery with 286 mg/l and least in the dairy effluents with 28mg/l. Based on the results obtained, there is need to treat effluents before discharging to water bodies.

**Keywords:** Bioprocessing effluents, Characterisation, Cations, and Physico-chemical parameters

### **1.0 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].

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.

## **2.0 MATERIALS AND METHODS**

### **2.1 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 Whatman 41 filter paper with diameter of 125 mm for the elimination of large materials and taken to the laboratory for analysis.

### **2.2 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<sub>5</sub>), pH, total solids (TS), total suspended solids (TSS), chemical oxygen demand (COD) and electrical conductivity<sub>4</sub> (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<sub>5</sub>, COD were determined based on standard methods [16]. Concentrations of CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup> 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.

### 2.2.1 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<sub>5</sub> after incubation for 5 days which corresponds to the final DO was recorded. BOD was calculated using Eq. (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.

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

### 2.2.2 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. There after 3.5ml 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 (1-2 drops) 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 Eq. (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.

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

### 2.2.3 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).

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

Total colour difference ( $\Delta E^*$ ) of the samples was calculated as shown in equation(4). In the equation,  $\Delta b^*$  is the blue/ yellow difference and  $\Delta a^*$  is the green/ red difference.

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

#### **2.2.4 Determining Cations in the Effluents**

To determine the phosphates ( $\text{PO}_4^{3-}$ ) 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 ( $\text{NO}_3^-$ ) 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 (0-10°C). 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 ( $\text{CO}_3^{2-}$ ) in the effluent, a 0.02N sulphuric acid was prepared and then mixed with 50 ml of each sample in a round bottomed 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 Eq. (5). In the equation, N is the normality of acid and A is the volume of acid.

$$C = \frac{(A) \times N \times 50000}{V} \dots\dots\dots(5)$$

To determine the concentration of sulphates ( $\text{SO}_4^{2-}$ ) 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.

### 3.0 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 <sub>5</sub> (mg/L)	1200±11	800±10	700±7	500
DO	1.24±0.4	0.81±0.1	5.20±0.2	-
CO <sub>3</sub> <sup>2-</sup> (mg/L)	28±0.3	80±0.8	287±0.5	-
SO <sub>4</sub> <sup>2-</sup> (mg/L)	40.80±0.4	52.76±0.1	49.51±0.5	-
PO <sub>4</sub> <sup>3-</sup> (mg/L)	0.37±0.04	0.11±0.01	0.38±0.06	30
NO <sub>3</sub> <sup>-</sup> (mg/L)	0.49±0.02	3.50±0.04	7.20±0.01	100

#### 3.1 Temperature, PH and Colour

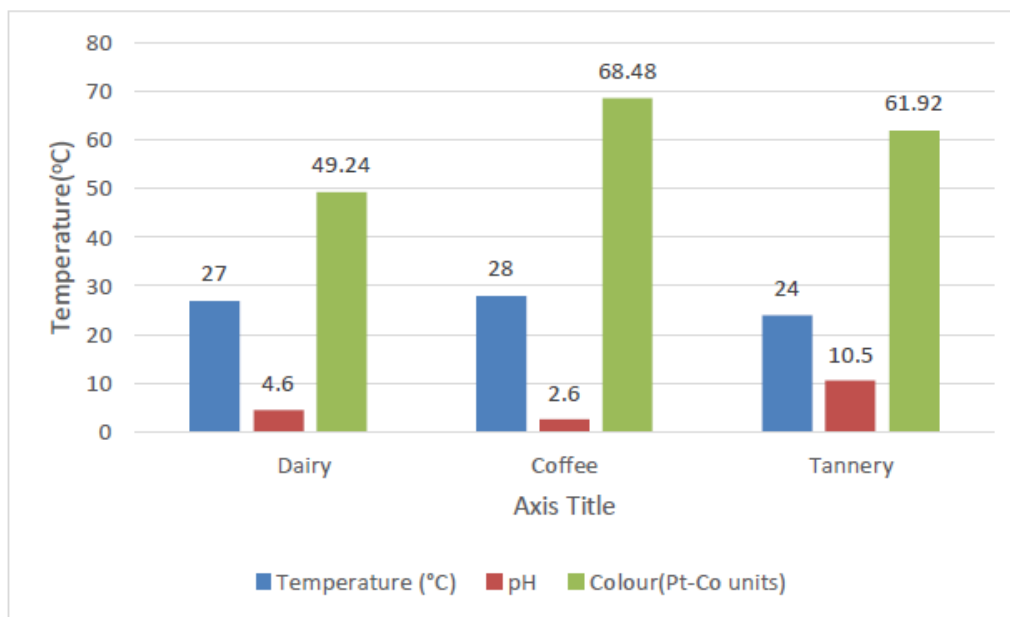


The results in Table 1 show that the minimum temperature of the effluents varied from  $24 \pm 0.1$  to  $28 \pm 0.1^\circ\text{C}$ . The highest temperature ( $28 \pm 0.5^\circ\text{C}$ ) corresponded to the coffee effluent, while the least ( $24 \pm 1.2^\circ\text{C}$ ) to the tannery effluents. The mean temperature for the dairy industry effluent was  $27 \pm 1^\circ\text{C}$ , 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  $40^\circ\text{C}$  [20- 22].

It was also observed that the pH values for the different effluents ranged from  $2.6 \pm 0.2$  to  $10.5 \pm 0.5$ . The effluents from coffee industries had the least pH ( $2.6 \pm 0.2$ ), which was well below the recommended standard cut off points. The highest mean value ( $10.5 \pm 0.5$ ) 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  $4.6 \pm 0.2$ , 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  $49.24 \pm 0.5$  and  $68.48 \pm 0.9$  Pt-Co units. Effluents from the coffee industry had the highest value of  $68.48 \pm 0.9$  Pt-Co units, followed by tannery with  $61.92 \pm 0.1$  Pt-Co units, and dairy came last with  $49.24 \pm 0.5$  Pt-Co units (Fig. 1).

**Fig. 1: Variation of temperature, pH, and colour of effluent for different bioprocessing industries.**

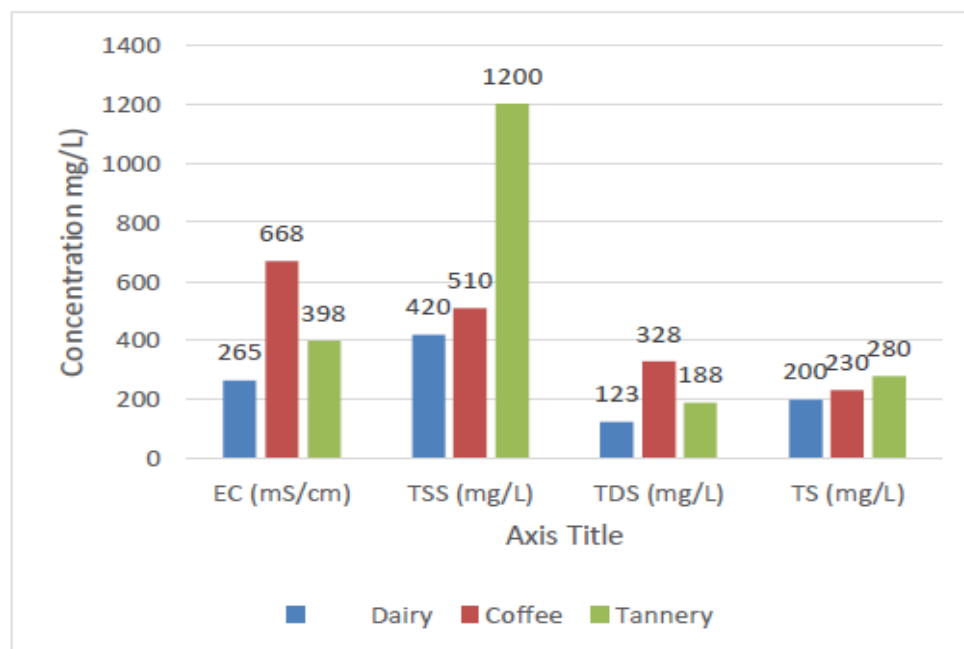




### 3.2 EC, TDS, TSS, and TS

The average electrical conductivity (EC) values for the effluents varied from  $265 \pm 5$  to  $665 \pm 10$  mS/cm, the highest being  $665 \pm 10$  mS/cm which corresponded to the coffee industry. The values for the tannery and dairy were  $75 \pm 1$  and  $265 \pm 5$  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  $123 \pm 3$  to  $328 \pm 1$  mg/L. The largest value of  $328 \pm 1$  mg/L corresponded to the coffee effluent while the least value of  $123 \pm 3$  mg/L to the dairy effluents while tannery effluents had a mean TDS of  $188 \pm 10$  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  $420 \pm 9$  to  $1200 \pm 1$  mg/L. The tannery effluent had the highest mean value of  $1200 \pm 1$  mg/L and this was followed by coffee ( $810 \pm 5$  mg/L) and dairy ( $420 \pm 9$  mg/L) effluents. As observed with the other parameter, the tannery effluent had the highest value mean value of  $280 \pm 3$  mg/L, and this was followed by coffee ( $230 \pm 6$  mg/L) and dairy ( $200 \pm 1$  mg/L) effluents (Fig. 2).

**Fig. 2: Variation of TSS, TDS, and TS concentration for different bioprocessing industries.**



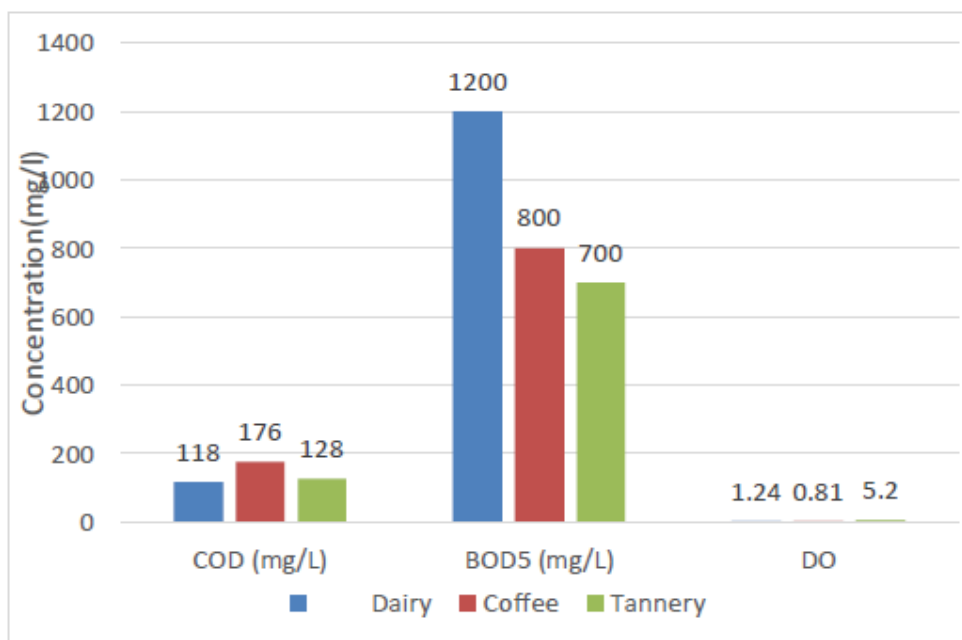
### 3.3 DO, COD and BOD<sub>5</sub>

The average values of COD and BOD<sub>5</sub> were  $118 \pm 5$  to  $176 \pm 1$  mg/L and  $700 \pm 6$  to  $1200 \pm 2$  mg/L,

respectively. The highest value ( $1200 \pm 2$ ,  $176 \pm 1$ ), 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  $1.24 \pm 0.01$ ,  $0.81 \pm 0.02$ , and  $5.20 \pm 0.2$  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, 24]. According to [25], the minimum levels of DO ( $\leq 4$  mg/L) present in the discharges were because of excessive natural contamination, showing an undeniable degree of  $BOD_5$  in the effluents (Fig. 3).

**Fig. 3: Variation of COD,  $BOD_5$ , and DO concentration for different bioprocessing industries**



### 3.4 $CO_3^{2-}$ , $SO_4^{2-}$ , $PO_4^{3-}$ and $NO_3^-$

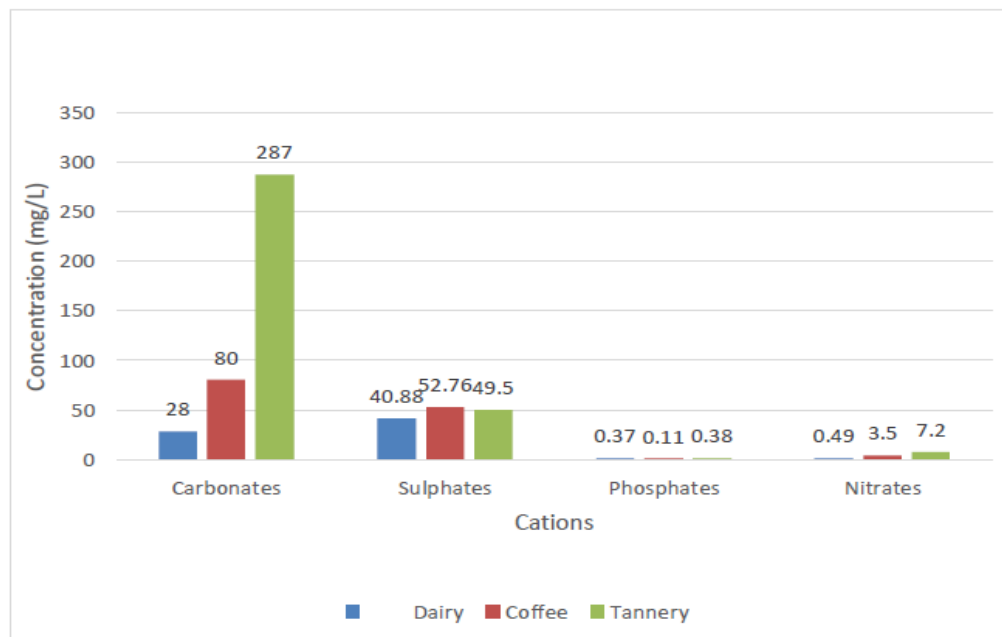
The  $CO_3^{2-}$  concentrations in the effluents from the three companies ranged from 280.5 to 286.9 mg/L on average (Fig. 4). Tannery effluents had the highest value of (286.9 mg/L), whereas dairy effluents had the lowest value of 28.5mg/L. The concentration of coffee effluents was 80.8 mg/L. The 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

The average  $\text{SO}_4^{2-}$  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  $\text{SO}_4^{2-}$  levels found in all effluents were lower than the recommended levels and therefore safe for release into the water body.

The mean  $\text{PO}_4^{3-}$  concentrations of effluents from tanneries portrayed the highest value of 0.380 mg/L, 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<sub>4</sub>mg/L. The  $\text{PO}_4^{3-}$  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  $\text{PO}_4^{3-}$  concentrations that were lower than the required<sup>4</sup> limits, making them safe for discharge into the surface of the water.

The values of  $\text{NO}_3^-$  in effluents from various industries were  $0.49 \pm 0.01$  to  $7.20 \pm 0.02$  mg/L. Tannery effluents had the highest concentration ( $7.20 \pm 0.02$ ), whereas dairy effluents had the lowest concentration ( $0.49 \pm 0.01$ ) and that of coffee effluents was  $3.50 \pm 0.04$ . All the  $\text{NO}_3^-$  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**



#### **4.0 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.

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