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Beverage Effluent Treatment Technology

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ABSTRACT: *A detailed beverage effluent treatment technology was developed in a period of 4 months, using samples from an operating beverage plant. The total number of samples collected were 1304. The volume of the sample collected hourly was 500ml for 4 hours to give a composite sample. The plant operated continuously for 6 days a week and had two-12 hour shifts a day. The technology consisted of four water treatment methods combined consecutively which were chemical, physical, biological and physical treatment methods. The aim of developing the technology was to reduce the sCOD, TSS and pH parameters to the required environmental specification. The untreated beverage wastewater has high solids content, high organic matter, and low pH which need pretreatment before it is discharged into the municipal sewage treatment works. The developed technology reduced the high solid content, high organic load and adjusted the pH to the required Bulawayo Municipality environmental specifications. The average percentage reduction in sCOD and TSS was 91.1% and 90.6% respectively. The pH was adjusted to 8.05. The obtained results indicated that the developed technology was effective for treating beverage wastewater at ambient temperature to meet the quality of effluent that can be discharged into public water works.*
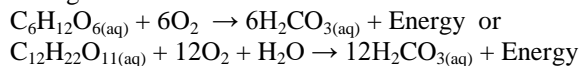**Keywords:** *Alkalinity, beverage effluent, buffering effect, sCOD.*

I. INTRODUCTION

The beverage industry holds a significant market share in the food industry with a market worth US$55 billion worldwide and it continues to show potential for growth[1]. Beverage manufacturing, however, comes with some unique challenges in the treatment of its effluent. The effluent from a beverage manufacturing plant is typically comprised of the following chemicals: sucrose, maltose, lactose, glucose, fructose, artificial sweeteners, fruit juice concentrates, flavouring agents, colouring agents, preservatives and mineral salts[2]. The beverage effluents may affect water quality in many ways, including organic matter increase in COD and BOD. The high organic load in the wastewater arises from dissolved sugars, colourants, flavours, preservatives and a high content of organic suspended solids, e.g. juice concentrate pulp. In order to control pollution and protect the environment, beverage effluent containing high concentrations of organic matter cannot be discharged to sewers and watercourses. The municipal authority in Bulawayo, Zimbabwe is placing severe restrictions on the quality of effluent which industry can discharge into their municipal system [3],[4]which makes on-site pre-treatment of beverage industry aqueous waste necessary before discharge to sewer. The aqueous waste emanates from syrup spillages associated with mixing, spillages in packaging, and wash and rinse water from the cleaning of tanks, equipment and bottle labelling sections. Stringent environmental regulations sanctionbeverage manufacturers from discharges that can negatively impact the environment but very few manufacturers treat their waste due to the high capital and maintenance costs of treatment [8]. Hence the validation and implementation of efficient, simple mitigation measures is indicated for compliance and environmental protection. This article describes the testing of a user friendly, highly efficient and innovative beverage aqueous waste treatment process.

II. THEORETICAL BACKGROUND

The main constituent of beverage industry liquid waste is sugar. This sub-class of carbohydrates[5]is highly biodegradable and is the primary contributor to bCOD (biodegradable COD), and the aqueous oxygen

depletion and eutrophication potential of the waste. The sugars potentially undergo a number of abiotic and biotic reactions such as the formation of carboxylic acid in the presence of oxygen [6], lactic acid an intermediate product of the oxidation of sugar, sugar inversion in the presence of H^+ ions [7] and fermentation (in anaerobic environments). The primary beverage waste sugars are $C_6H_{12}O_6$ monosaccharides or $C_{12}H_{22}O_{11}$ disaccharides. The complete mineralization of these aqueously dissolved sugars in the presence of oxygen releases energy through the reaction:

$C_6H_{12}O_{6(aq)} + 6O_2 \rightarrow 6H_2CO_{3(aq)} +$ Energy or

$C_{12}H_{22}O_{11(aq)} + 12O_2 + H_2O \rightarrow 12H_2CO_{3(aq)} +$ Energy

The carboxylic acid generated decreases pH of the solution resulting in a very acidic post-reaction condition. The lactic acid which is an intermediate product of the for-mentioned reaction and the acid based flavours also contribute to the acid conditions of the effluent. The high TSS levels in the effluent are mainly contributed by the pulp from the juice concentrates and coagulation products formed by the destabilisation of acid-based flavours and colourants upon addition of the detergents used in cleaning the equipment which results in the formation of the scum[9]The characteristics of the beverage effluent are similar to the characteristics of a brewery or sugar industrial effluent. The effluents from these industries also have high sugar contents resulting in very high COD and TSS and very low pH [10, 11, 12, 13,14,15,16, 17]. The technologies most commonly used for the treatment of the effluents with high sugar content involve biological water treatment methods such as the use of biodigestors and lagoons[18, 19,20,21,22]. These biological processes seldom have efficiencies above 90%; require considerable expertise to operate; are subject to temperature, shock loading and toxic substance inhibition; require a large surface area for installation; and the treatment times of more than 2 days necessitate large volumes of on-site tankage and greater risk of plant flooding. In regard to these challenges, a user friendly, highly efficient and innovative beverage effluent treatment technology was targeted for development and bench testing. This technology consists of 4 stages incorporating physical, chemical and biological [23, 24] water treatment processes as shown in Figure 1.
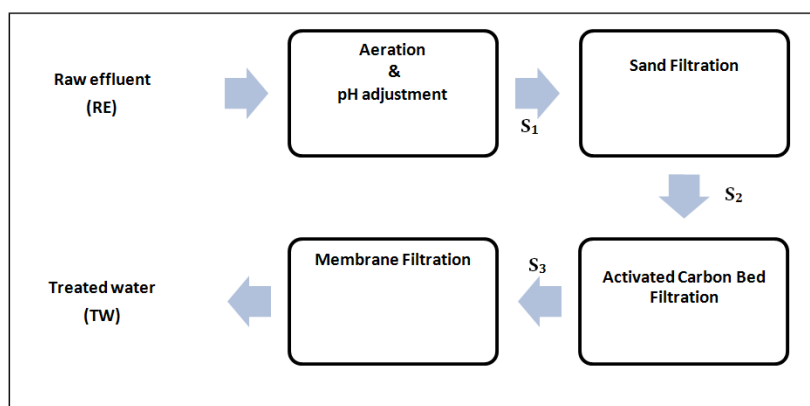

Figure 1 Block diagram of beverage effluent treatment technology

The block diagram in Figure 1 shows the beverage effluent treatment technology. The flow of the treated effluent from one stage to the next is designated by S_n where S denotes the outflow from a stage and n denotes the stage number. The processes shown in Figure 1 are fully explained below.

First Stage (Aeration and pH Adjustment)

The first stage, chemical treatment, is responsible for the oxidation of the sugars and elimination of odours by aeration[6] and for adding lime to adjust pH [25] and the promotion of coagulation. Air is blown in continuously from the moment the effluent gets into the reactor. The change in pH destabilises the acid based colourants and flavours[9] resulting also in the removal of the colour of the effluent upon subsequent coagulation and sedimentation. The destabilisation of the colourants and the flavours in the presence of the lime will also result in the formation of aggregates[9].

Second Stage (Sand Filtration)

The second stage, sand filtration,is a physical treatment to remove suspended solids.

Third Stage (Activated Carbon Bed Filtration)

In this stage there is activated carbon adsorption, predominantly of organics, for the removal of COD, odour and colour [26].

Fourth Stage (Filtration)

The final stage is a physical treatment stage of (micro) filtration membrane for the removal of minute particles remaining suspended in the treated effluent. To the best of our knowledge and literature reviewdone, the technology detailed here has never been used for beverage effluent aqueous waste treatment. This technology was tested in the laboratory and the method used and results obtained are detailed in the following sections.

III.　　METHOD

3.1 Equipment
The following equipment were used:
1.　Vacuum Filtration unit (sand filter, Whatman filter paper 50µm)
2.　pH meter (Eutech Instruments pH 700 Bench Meter, Serial No: 734632)
3.　Aeration unit (air was blown (purging) through a glass tube of 3mm inside diameter immersed into the solution up to a depth of 9/10th of the height of the reactor from the bottom)
4.　1 Litre Beakers

3.2 Reagents
The following reagents were used:
1.　Lime
2.　Activated Carbon
3.　Sand

3.3 Sampling
The raw effluent was collected from an existing, large-scale, beverage manufacturing plant in Zimbabwe. The sampling period lasted for 4 months. 500ml samples were collected every hour for 4 hour to give a composite sample for each 12 hour shift. This plant operates for 24 hours for 6 days a week and the 7th day, mainly Sundays, are reserved for plant maintenance. Therefore the total number of samples collected were 2304 and the total number of composite samples were 576. NB Each shift produces a different brand of beverage. (The effluent samples collected were Orange, Rasberry, Cream-Soda and clean in place (CIP) wastewater). In this line of production, the company produces equal volumes of each brand. The aforementioned sampling procedure was carried out in every shift and general cleaning was carried out after every shift.The measurement of pH was done in situ,

3.4 Raw Effluent treatment
The raw effluent collected from the plant was sequentially treated using the following stages.

3.4.1 First Stage
1.　500ml of raw effluent was poured into a 1L beaker.
2.　The effluent was agitated using a magnetic stirrer at a rate of 100rpm for 10 minutes
3.　The effluent was aerated by blowing air through a glass tube of 3mm inside diameter immersed into the solution up to a depth of 9/10 th of the height of the reactor at a flow rate of $5.6\times10^{-3}\text{m}^3/\text{s}$ whilst agitating resulting in an total oxygen loading of 1,570 mg O_2/L•s .
4.　The pH of the mixture was adjusted using lime until a constant pH of 10.5 was achieved and the solution laid to rest for 5 minutes
5.　After 5 minutes the pH was rechecked to ensure it was at 10.5. In all samples additional pH adjustment was not needed to return to 10.5.

3.4.2　Second Stage
1.　The mixture from 3.4.4 1 was passed through a sand filter bed with grains with a D60/D10 = 1.9

3.4.3 Third stage
1.　Activated carbon (DCN 800) was poured into a beaker forming a bed whose thickness is 1/3 of the total height (~400 mL of GAC) of the beaker.
2.　The filtrate obtained from 3.4.2 was poured into the bed.
3.　The filtrate was left in the bed for a period of 4 hours without agitation.

3.4.4 Fourth stage
1.　The solution obtained in 3.4.3 iii was decanted and filtered using Whatman Filter paper (50 microns)
2.　The filtrate obtained from 3.4.4 i is the treated water (TW) and this is the sample to be analysed for sCOD, TSS and pH.

3.5 Analytical Tests

Chemical analyses were conducted on samples of the raw effluent (RE), intermediate stages (S1, S2, S3) and treated water (TW). The following parameters were analysed on RE, S1, S2, S3 and TW as described in Standard Methods[28]: sCOD, TSS and pH. The weekly average results of the sCOD, TSS and pH obtained from section 3.4 are fully analysed and discussed in the following subsections.

IV.   RESULTS AND ANALYSIS

4.1 *pH Analysis*

The results in Table 1 illustrate the monthly average pH of the effluent obtained from weekly averages before, after and at each stage of treatment.

Table 1 Results of inter stage effluent pH treatment.

Brand Sample	Monthly					
		RE	S$_1$	S$_2$	S$_3$	TW
	1	3.01	10.5	7.23	7.75	7.60
	2	3.09	10.5	7.19	8.05	7.65
Orange	3	2.98	10.5	7.27	8.10	7.49
	4	3.02	10.5	7.19	8.3	7.61
	Average	3.03	10.5	7.22	8.05	7.59
	5	2.86	10.5	7.13	8.23	7.50
	6	2.98	10.5	7.16	8.00	7.40
Raspberry	7	3.1	10.5	7.15	8.06	7.70
	8	3.12	10.5	7.2	8.08	7.86
	Average	3.02	10.5	7.16	8.09	7.62
	9	3.00	10.5	7.18	7.99	7.53
	10	3.30	10.5	7.05	8.00	8.74
Cream soda	11	3.60	10.5	7.17	8.08	8.87
	12	3.23	10.5	7.25	8.05	8.35
	Average	3.28	10.5	7.16	8.03	8.37
	13	3.50	10.5	7.21	8.15	8.90
	14	3.20	10.5	7.19	8.07	8.17
CIP wastewater	15	3.60	10.5	7.14	8.01	8.90
	16	3.40	10.5	7.09	8.00	8.50
	Average	3.43	10.5	7.16	8.06	8.62
Overall Ave.		**3.19**	**10.5**	**7.18**	**8.06**	**8.05**

The results in Table 1 indicate that the pH of the raw effluent is very low - the effluent is very acidic. The average raw effluent pH was found to be 3.19. The acidity of the effluent is mainly contributed by the presence of sucrose which is the main constituent of the beverage which undergoes oxidation resulting in the formation of carbon dioxide and water. The carbon dioxide produced in the presence of water results in the formation of carbonic acid. The incomplete oxidation of the sugar, sucrose, can also result in the production of lactic acid. The acid-based flavours and colourants also contribute to the acidity of the effluent. The chlorine (added as HOCl) used as a disinfectant in the presence of water creates acidic conditions hence increasing the acidity of the effluent.

The results also illustrate that the pH of the raw effluents vary according to the brand being manufactured. The effluent of the orange brand has a low pH of 3.02 on average as compared to the pH of other brands which are for 3.02, 3.28, and 3.43 for Raspberry, Cream soda and CIP wastewater respectively. The low pH of the orange effluent is due to the presence of additional organic acids such as citric acid present in juice concentrates. The CIP waste water has got a slightly higher pH compared to the other 3 brands because of the caustic soda added during washing which neutralises the acids.

4.1.1 Alkalinity

Alkalinity is the buffering capacity of a water body and it provides a measure of the ability of a water body to neutralize acids and bases thereby maintaining a fairly stable pH. In order to be a good buffer, compounds such as bicarbonates, carbonates, and hydroxides can be added to aqueous wastewater stream as these species combine with H+ ions thereby neutralizing the pH. In this research work, the buffering capacity was enhanced by the addition of lime and the results of the carbonates, bicarbonate, hydroxyl ions present are shown in Table 2 in the supplementary notes (NB the chemistry and the derivation of the equations for the total alkalinity are well detailed in the supplementary notes.)The results in Table 2 illustrate that the concentrations of bicarbonates, carbonates and hydroxyl ions are negligible indicating that the concentrations of the carbonic acid formed in this effluent is very negligible. This is contributed by the fact that the retention time in the reactor is very minimal for complete oxidation of the sugars and for the absorption of CO$_2$ from the atmosphere into the

effluent for the formation of the carbonic acid. Therefore, in conclusion there is very negligible concentration of carbonic acid which contributes to low pH of the effluent. Hence it can be concluded that the low pH of the effluent is due to the acid based flavours, acid based colourants and lactic acid present in the effluent.

4.2 TSS Analysis

Table 2 shows the results of TSS characterization and its relative removal. The column and line graph shown in Figure 2 was constructed by results from Table 2 for comparison of the different brands.

Table 3 Results of inter stage effluent TSS treatment

| Brand Sample	Sample No.	TSS (ppm)					% Reduction				Overall Efficiency (%)
		RE	S1	S2	S3	TE	1st Stage	2nd Stage	3rd Stage	4th Stage	
	1	1800	2548	305	416	185	-41.6	88.0	-36.4	55.4	89.7
	2	2056	2857	300	405	176	-39.0	89.5	-35.0	56.5	91.4
Orange	3	1990	2826	283	390	178	-42.0	90.0	-37.8	54.4	91.1
	4	1880	2632	292	400	179	-40.0	88.9	-37.0	55.4	90.5
	Average	1931.5	2715.8	295.0	402.8	179.5	-40.7	89.1	-36.6	55.4	90.7
	5	845	1190	135	185	84	-40.8	88.7	-37.0	54.6	90.1
	6	908	1267	144	197	90	-39.5	88.6	-36.8	54.3	90.1
Rasberry	7	756	1073	112	153	70	-41.9	89.6	-36.6	54.2	90.7
	8	678	949	99	134	60	-40.0	89.6	-35.4	55.2	91.2
	Average	796.8	1119.8	122.5	167.3	76.0	-40.6	89.1	-36.5	54.6	90.5
	9	906	1268	152	206	93	-40.0	88.0	-35.5	54.9	89.7
	10	654	910	100	137	61	-39.1	89.0	-37.0	55.5	90.7
Cream soda	11	456	638	66	90	40	-39.9	89.7	-36.4	55.6	91.2
	12	547	761	78	107	48	-39.1	89.8	-37.2	55.1	91.2
	Average	640.8	894.3	99.0	135.0	60.5	-39.5	89.1	-36.5	55.3	90.7
	13	990	1380	155	212	96	-39.4	88.8	-36.8	54.7	90.3
	14	1010	1405	154	210	96	-39.1	89.0	-36.4	54.3	90.5
CIP wastewater	15	1200	1693	188	256	112	-41.1	88.9	-36.2	56.3	90.7
	16	856	1200	139	190	87	-40.2	88.4	-36.7	54.2	89.8
	Average	1014.0	1419.5	159.0	217.0	97.8	-40.0	88.8	-36.5	54.9	90.3
						Ave.	-40.2	89.0	-36.5	55.0	90.6
						Std D.	1.0	0.6	0.7	0.7	0.6
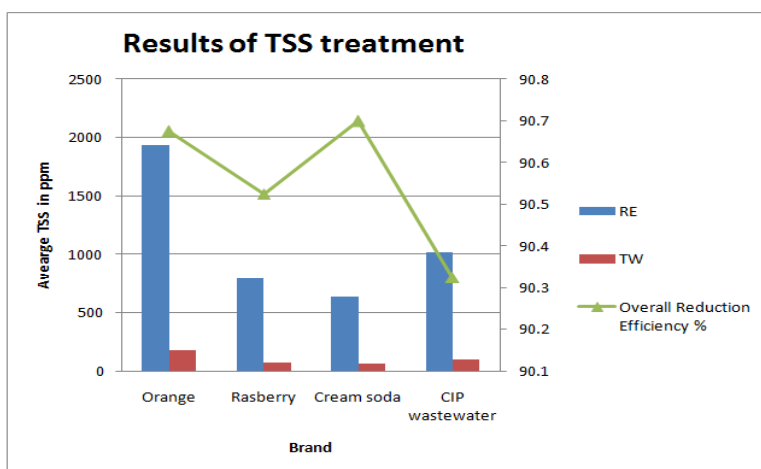
Figure 3 Graph of Average TSS and % TSS reduction against brand wastewater

The TSS results for the raw effluent are characterised by very high values in all four effluent brands ranging from 547 to 2056 ppm and these values are non-compliant with the EMA and local authority specifications of TSS < 600ppm. The high TSS value from the analytical results coincide with the opaqueness and turbidity observed in the physical/visual inspection. The high TSS of the effluent can mainly be explained by the presence of colourants and flavours and the precipitation of some chemical elements in the presence of caustic soda and detergent associated with the cleaning processes. As shown in Figure 2, the effluent obtained during the orange flavoured beverage production showed higher TSS values compared to the other samples collected due to the additional contribution of the pure orange juice pulp. After treatment it can be observed that that all the brands have TSS values that are more or less the same save for the orange flavour with a slightly higher value. Figure 2 also shows that the overall reduction efficiency is approximately the same in all 4 brands.

The results in Table 2 show an increment in the suspended solids after treatment in the first stage. The TSS values range from 638 – 2857 ppm. This increase is attributed to the lime added which promotes aggregation of otherwise colloidal particles as well as potential hydroxide and carbonate precipitates which both

add to the suspended solids. The average increase in suspended solids was found to be 40.2 %. In the second stage (filtration) after treatment the TSS was reduced to a range of 66- 305 ppm. The decrease is due to the fact that during filtration the suspended particles were trapped in the filter bed. The percentage TSS reduction was found to be 89.0 %. In the third stage after treatment the TSS increased ranging from 90 – 416 ppm. The increase in the TSS at this stage is attributed to continuation of the coagulation/flocculation process initiated in stage 1, and the generation of minute particles (fines) resulting from the disintegration of the activated carbon. The average increase in TSS was found to be 36.5 %. In the fourth stage, the results in Table 2 clearly illustrate a decrease in the TSS values after membrane filtration. The decrease in TSS is mainly due to the fact that a significant fraction of the micron-size particles from the previous stage are trapped during filtration. The average % TSS reduction was found to be 55.0%.

In this treatment train it can be observed that the second and third stages contribute to increases in the TSS values but due to the much higher second and fourth stage removals of suspended solids the net process removal is excellent. The overall % reduction of the TSS is 90.6%.

4.3 *sCOD Analysis*

The sCOD results of the experiments carried out in section 3.4.4 are shownin Table 3 and the graph in Figure 3 was constructed using the results in Table 3.

Table 4 Results of interstage effluent sCOD treatment

| Brand Sample	Sample No.	COD (ppm)					% Reduction				Overall Efficiency (%)
		RE	S1	S2	S3	TE	1st Stage	2nd Stage	3rd Stage	4th Stage	
	1	13 865	12745	4219	1497	1108	8.1	66.9	64.5	26.0	92.0
	2	23890	22066	7 284	2574	1922	7.6	67.0	64.7	25.3	92.0
Orange	3	19900	18380	6066	2137	1591	7.6	67.0	64.8	25.5	92.0
	4	17986	16665	5498	1959	1480	7.3	67.8	64.4	24.5	91.8
	Average	20592	17464	5261	2041.75	1525.25	7.65	67.175	64.6	25.325	91.95
	5	17688	16333	5393	1914	1435	7.7	67.0	64.5	25.0	91.9
	6	18456	17053	5630	1980	1476	7.6	67.0	64.5	25.5	92.0
Rasberry	7	15678	14450	4777	1687	1276	7.8	66.9	64.7	24.4	91.9
	8	18345	17044	5593	1990	1482	7.1	67.2	64.4	25.5	91.9
	Average	17541.75	16220	5348.25	1892.75	1417.25	7.55	67.025	64.6	25.1	91.925
	9	16576	15316	5064	1794	1350	7.6	66.9	64.6	24.7	91.9
	10	15678	14500	4800	1710	1290	7.5	66.9	64.4	24.6	91.8
Cream soda	11	18031	16768	5500	2000	1505	7.0	67.2	63.6	24.8	91.7
	12	16789	15513	5112	1917	1408	7.6	67.0	62.5	26.6	91.6
	Average	16768.5	15524.25	5119	1855.25	1388.25	7.425	67	63.775	25.175	91.75
	13	9215	8514	2809	998	753	7.6	67.0	64.5	24.5	91.8
	14	11666	10799	3560	1257	937	7.4	67.0	64.7	25.5	92.0
Rinse water	15	4980	4600	1510	539	400	7.6	67.2	64.3	25.8	92.0
	16	14567	13459	4450	1580	1166	7.6	66.9	64.5	26.2	92.0
	Average	10107	9343	3082.25	1093.5	814	7.55	67.025	64.5	25.5	91.95
						Ave.	7.6	67.1	64.4	25.3	91.9
						Std D.	0.3	0.2	0.6	0.7	0.1
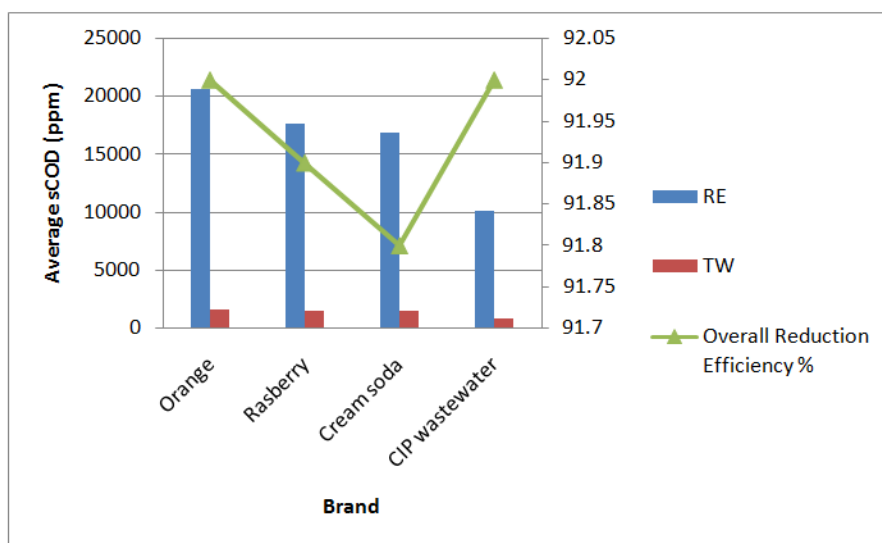
Figure 4 Graph of Average sCOD reduction against brand wastewater

Table 3 results indicate that very high sCOD values in the raw effluent. These sCOD values range from 4980 – 23890 ppm. These values do not comply with the Bulawayo City Council specifications of COD less than 2000ppm. These high sCOD values are attributed to the high concentration of sugars, colourants and flavours used in the manufacturing of the beverage. In the first stage after treatment the sCOD values decreased by an average of 7.6 % and the sCOD were in the range of 4600 – 22066 ppm. The decrease in the sCOD values in this stage is mainly attributed to the aeration carried out in the first stage of the treatment whereby the air attributes to the complete oxidation of the sugars to carbon dioxide and water. In the second stage, the results indicate a significant decrease in the sCOD value of % average of 67.1% with the sCOD ranging between 1510 – 7284 ppm. In the third stage of treatment there is again a significant decrease in sCOD in the range 539 – 2574ppm. The decrease in the sCOD values at this stage is mainly due to continuous oxidation of the sugars, aerobic digestion which occurs at this stage, adsorption of sCODon the activated carbon that was of sufficiently small size fraction or dissolved to pass through the stage 2 sand filtration. In the fourth stage, the decrease is less than in the second and third stage having a % average of 25.3 % leaving the sCOD in the range of 400 – 1922ppm. This decrease in sCOD is due to the continuous oxidation of the sugars from the previous stages, the continuous removal of suspended solids, including sCOD which remained sorbed on the suspended solids and minute activated carbon particles that are physically excluded by the membrane filtration.

In Figure 3, it can be observed that the orange wastewater has the highest sCOD compared to the rest due to the presence of the juice concentrates which contain pulp as well as other organic acids. The sCOD for orange wastewater is on average 20592 ppm and 17542ppm, 14567ppm and 16769ppm for raspberry, cream soda and CIP wastewater respectively. The CIP wastewater has a relatively less sCOD values because its organic fraction is considerably less concentrated due to it being dilute.

The overall % reduction of the sCOD for this treatment technology was found to be 91.1 %. This high % sCOD reduction clearly indicates that this beverage effluent technology is highly efficient. The high efficiency of this treatment technology can be maintained by ensuring that back-wash using water and caustic soda is carried out approximately twice per day (once per shift) and that the GAC mass is maintained by fresh carbon replacement of fines lost through inevitable disintegration of grain size with use and backwashing. The backwashing maintains bed permeability by removing filtered particles and decompacting the bed, while the caustic increases organics solubility and adds a high concentration competitive adsorbate (OH-) which together regenerate the GAC adsorption capacity. For initial feasibility evaluation the fines loss rate is estimated as 4% per backwash/regeneration cycle based on published literature [29]. Consequently, it is estimated addition of fresh GAC equal to about 15% of the bed mass will be required every fourth shift.

V. CONCLUSION

The developed beverage effluent treatment technology reduced the organic load (sCOD) and TSS by 91.1% and 90.6 % respectively and pH was adjusted from an average of 3.19 to 8.05 which are permissible levels required by the Bulawayo City Council. The adjustment of the sCOD, TSS and pH values to be compliant with the specifications of EMA and the City Council imply that the sewer and discharge violation charges will be lower resulting in significant savings to the industry. Although not investigated in this study, another benefit to the plant could be realised by further treatment of the treated effluent by disinfecting and reusing it in the plant. In regard to aforementioned conclusions it can be concluded that this beverage effluent treatment technology is highly efficient, user friendly and innovative.

ACKNOWLEDGEMENTS

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Supplementary notes

$$pH = -log_{10}[H^+] \qquad (1)$$

$$[H^+] = 10^{-pH} \qquad (2)$$

$$[OH^-] = 10^{pH-14} \qquad (3)$$

$$CO_2(g) + H_2O\ (l) \rightarrow H_2CO_3(aq) \qquad (4)$$

$$K_1 = \frac{[H_2CO_3]}{[CO_2][H_2O]} \qquad (5)$$

$$\therefore [CO_2] = \frac{[H_2CO_3]}{K_1}$$

$$H_2CO_3(aq) \leftrightarrow HCO_3^{-1} + H^+ \qquad (6)$$

$$K_2 = \frac{[HCO_3^{-1}][H^+]}{[H_2CO_3]} \qquad (7)$$

$$\therefore [H_2CO_3] = [10^{-pH}]\frac{[HCO_3^{-1}]}{K_2}$$

$$HCO_3^{-1} \leftrightarrow H^+ + CO_3^{-2} \qquad (8)$$

$$K_3 = \frac{[CO_3^{-2}][H^+]}{[HCO_3^{-1}]}$$

$\therefore [CO_3{}^{-2}] = \frac{K_3[HCO_3{}^{-1}]}{[H^+]}$

(4) + (6):

$CO_2(\text{g}) + H_2O(\text{l}) \rightarrow HCO_3{}^{-1} + H^+$
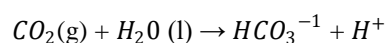
$K = K_1 \times K_2$

$K = \frac{[HCO_3{}^{-1}][H^+]}{[CO_2][H_2O]}$

$[CO_2] = P_{CO_2}/K_h$

$[HCO_3{}^{-1}] = \frac{K[P_{CO_2}/K_h]}{[H^+]} = \frac{K[P_{CO_2}/K_h]}{[10^{-pH}]}$

$P_{CO_2} = 390 \times 10^{-6}$ atm (partial pressure of CO_2 in air)
$K_h = 29.76$ atm/(mol/L) at 25°C

$K_1 = $ 1.70E-03
$K_2 = $ 4.60E-07
$K = K_1 \times K_2 = $ 7.82E-10

	pHRE	[H+]RE	[OH-]RE	[CO2]RE	[HCO32-]RE	[CO32-]RE	pHES1	[H+]ES1	[OH-]ES1	[CO2]ES1	[HCO32-]ES1	[CO32-]ES1	Δ[OH-]RE-ES1
1	3.01	0.000977	1.02329E-11	1.31048E-05	3.405E-15	1.63397E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
2	3.09	0.000813	1.23027E-11	1.31048E-05	3.316E-15	1.91361E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
3	2.98	0.001047	9.54993E-12	1.31048E-05	3.439E-15	1.54026E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
4	3.02	0.000955	1.04713E-11	1.31048E-05	3.393E-15	1.6665E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
5	2.86	0.00138	7.24436E-12	1.31048E-05	3.583E-15	1.21743E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
6	2.98	0.001047	9.54993E-12	1.31048E-05	3.439E-15	1.54026E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
7	3.1	0.000794	1.25893E-11	1.31048E-05	3.306E-15	1.95186E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
8	3.12	0.000759	1.31826E-11	1.31048E-05	3.285E-15	2.03075E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
9	3	0.001	1E-11	1.31048E-05	3.416E-15	1.6021E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
10	3.3	0.000501	1.99526E-11	1.31048E-05	3.105E-15	2.90601E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
11	3.6	0.000251	3.98107E-11	1.31048E-05	2.847E-15	5.31507E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
12	3.23	0.000589	1.69824E-11	1.31048E-05	3.173E-15	2.52702E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
13	3.5	0.000316	3.16228E-11	1.31048E-05	2.928E-15	4.34253E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
14	3.2	0.000631	1.58489E-11	1.31048E-05	3.202E-15	2.38046E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
15	3.6	0.000251	3.98107E-11	1.31048E-05	2.847E-15	5.31507E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228
16	3.4	0.000398	2.51189E-11	1.31048E-05	3.014E-15	3.55085E-22	10.5	3.16E-11	0.000316	1.31E-05	9.76E-16	1.44751E-15	0.000316228