Original Paper

Treatment and Characterization of Wastewater from Tissue

Paper Making Industry Using Bamboo as Raw Material

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Abstract

This article focused on the treatment and characterization of wastewater from tissue paper making industry located in Akwalbom State which uses bamboo as raw material. The wastewater samples generated during the pulping and bleaching processes were collected, analyzed to determine the pollution loads and thereafter treated to ascertain its suitability for disposal into the environment using standard methods by American Public Health Association (APHA). The results obtained before treatment were pH (7.42 and 4.49), EC (316 μ S/cm and 47 μ S/cm), TDS (158mg/l and 24mg/l), Turbidity (19.3NTU and 28.7NTU), BOD₅ (74.02mg/l and 62.00mg/l), COD (140.30mg/l and 120.40mg/l), TOC (10.3% and 7.1%), selected heavy metals like, Pb (0.281mg/l and 0.273mg/l), Ni (0.115mg/l and 0.117mg/l), and Co (0.193mg/l and 0.208mg/l). The corresponding values after treatment were pH (8.08 and 7.88), EC (4.00 μ S/cm and 4 μ S/cm), TDS (2.00mg/l and 2mg/l), TUrbidity (9.6NTU and 5.1NTU), BOD₅ (4.06mg/l and 4.11mg/l), COD (14.20mg/l and 12.80mg/l), TOC (0.1% and 0.1%), with selected heavy metals like Pb (0.040mg/l and 0.041mg/l), Ni (0.003mg/l and 0.005mg/l) and Co (0.011mg/l and 0.015mg/l). The average extent of treatment was slightly above 70% for the pulping unit sample and about 80% for that from the bleaching unit. The study recommends wastewater treatment before disposal.

Keywords

treatment, characterization, wastewater, extent of treatment, tissue paper, bamboo, pulping, bleaching

1. Introduction

Waste is described as "any substances, solid, liquid or gaseous that remains as residue or an incidental by-product of manufacturing for which no use can be established by the organization or system that produces it" (Isirimah, 2002). It is described by Tchobanoglous et al. (1993) as any unavoidable material resulting from domestic activity or industrial operation for which must be discarded. Industrial processes produce liquid, solid and gaseous wastes which can have negative impacts on the environment including people. These wastes are generated either during processing or at the end of the production process (Nebel & Wright, 1999). In order to minimize risks, waste matter and energy contained in the industrial wastes, treatment is needed to increase the efficiency and profitability of industry (Elhaj, 1984). Tissue paper, often known as tissue, is a thin, lightweight paper created from recycled pulp or virgin wood pulp. (Nanko et al., 2005). Tissue paper is produced using a variety of fiber types, example is fibre sourced from bamboo. The nature of bamboo employed for making tissue is the dry Bamboo (Moso Phyllostachysedulis). It is a biomass, characterized by long and semi-long fibers similar to hard and soft woods (Lewis & Carol, 2008), with higher fines percentage, density and resistance to storage degradation than other fibers. Bamboo has culms and internodes (most desirable source of fibers) and possesses the capability to absorb twice the measure of carbon as trees. It has natural antibacterial properties while the decomposing discarded leaves provide nutrients needed for growth (Phillips et al., 2015). Tissue paper making procedure from Bamboo (Phyllostachysedulis) is simple and straightforward but generates bulky wastes; solid, particulates, liquid waste and gaseous waste/emission (Akpan, 2021). This is because of the high energy, virgin fiber pulp and water it requires (Paulapuro, 2000). Every unit/processes employed in the conversion of bamboo into tissue paper generates waste of diverse types, These wastes, especially liquid waste (due to the large quantity of water employed in the different process units) are of immense concern owing to the toxic nature arising from harmful chemicals employed in the conversion processes. This waste therefore needs to be assessed, treated independently and re-characterized to ascertain the composition of the wastewater discharged into the host community inland waters and land.

2. Method

2.1 Tissue Paper Making Process

This study involves the use of dry bamboo; Moso bamboo (Phyllostachysedulis) for the production of tissue paper (Figure 1). The bamboo was cut into sizes of 10-25 mm and crushed into tiny fine particles by the crushing machine and then conveyed to the digester for pulping. The digester contains a solution of water, caustic soda, and ammonia. A variety of chemicals are added to the system at different stages to enable the finished tissue paper have unique features like strength, brightness, softness, shade and thickness (Kan & Wong, 2015). The pulp is allowed to ferment so that hemicelluloses and lignin can decompose producing more cellulosic pulp and then channeled to the boiler which cooks the bamboo into charf and fibre (black fibre) using a mixture of caustic soda and ammonia (black liquor). The

boiler boils the bamboo pulp in water that has been previously treated with industrial salt (Nacl). Also, steam is used to rapidly transport fine fibres to the mixer (production pool). A lot of wastewater containing a combination of caustic soda and ammonia (black liquor) are generated and discharged into the environment.

The black pulp fibres are washed by chemicals introduced into the digester and are vibrated and passed through a vibrating screen, which allows only fine fibers passage while charfs in addition with impurities are trapped. The fibres are later returned to the crushing machine for a second crushing phase to soften the fiber and therefore produce finer fibers. A portion of the wastewater is recycled and returned to the digester while the fibers are transported to the bleaching section where hypochlorite is added to whiten the fibers. Pulp bleaching is used to advance the whiteness of the bamboo pulp, maintain its strength, and prevent pollution. Wastewater with bleaching agents (chlorine) are also generated and discharged. Again, after bleaching, the fibers are washed again to remove the bleaching chemicals thereby generating more wastewater. The finely white pulp fibres (stock) are sent to the mixer at high speed using steam and water to the production pool for stock preparation. The pulp is stirred together with a dispersant or dispersing agent (usually a surfactant), that is added to a molten or liquid suspension, like a colloid or emulsion, to enhance particle separation and prevent their settling or clumping (Pirrung et al., 2002). Some of the water is removed by drying on steam heated cylinders with felts which generates the steam that is fed into the pool. The produced tissue is then peeled away from the mother rolls with a knifelike object and wrap into a jumbo reel in a cone. The rewinder machine receives the master or jumbo reels. The rolls are then cut into sizes, samples are gathered and examined for quality control compliance, and the product is subsequently packaged for sale.

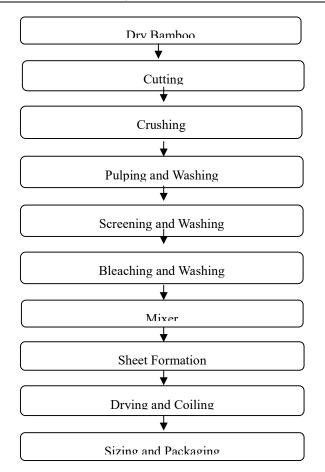


Figure 1. Flow Chart for Tissue Paper Making from Bamboo

2.1.1 Wastewater Collection and Handling

Two wastewater samples from the bamboo based tissue paper factory were collected with the aid of 1000ml glass bottles, properly labeled, stored in icepack, transported to the laboratory and analyzed. These wastewater samples were generated during the pulping process in the digester and the ones generated in the bleaching unit. The samples were subjected to chemical, physical, and biological testing.

2.1.2 Equipment

The following equipment/apparatus were employed in the analysis: oven, reflux tube/digestion flask, electro-thermal heater and buckner flask. Others were HANNA Multi-parameter meter (HI9829), AAS (Atomic Absorption Spectrophotometer and digital weighing balance. Auto clave, multi-parameter photometer and desiccator were also used.

2.1.3 Analytical Procedures

The Federal Ministry of Environment (FMEnv), and the American Public Health Association (APHA) standard methods for the examination of water and wastewater (APHA, 2012) were used for the analysis. Below are the specific procedures for the different analyses carried out on the pulping and bleaching wastewater samples:

a. Determination of pH, Conductivity, Temperature and Total Dissolved Solids

The pH, electrical conductivity, temperature, and Total Dissolved Solids (TDS) of the wastewater samples from the two units were determined by direct measurement using multi-parameter data logger (multi 340i/set) comprising a pH meter (Hanna HI-8424), conductivity meter (Hanna HI-9835) and TDS meter (Hanna HI-9146). The meters were respectively calibrated prior to use with buffer standards as required by instrument manufacturers using potassium chloride solutions and zero oxygen solution (both from HACH). The different meter probes were dipped directly and repeated three times into each test sample one after the other then the readings displayed on the screens were recorded after stabilization. The probes were rinsed in distilled water after each measurement and the display modes attuned to standard to avoid compromising the next sample to be tested.

b. Turbidity Measurement

The turbidity levels of the wastewater samples were determined by Nephelometric method using 2100Q HACH Turbid-meter in accordance with APHA 2130B (APHA, 2012). The meter was calibrated with formazin standard solution of 20, 100 and 800 Nephelometric transfer unit, NTU, from HACH. Each liquid sample was put into a cuvette and placed for measurement in the sample holder. Turning a dial knob to display the reading in NTU yielded the turbidity value.

c. Biochemical Oxygen Demand Measurement

Samples of the wastewater and dilution water were mixed thoroughly while avoiding violent agitation. Two 300mL BOD bottles were filled with the diluted sample. Two other 300mL BOD bottles were as well filled with the dilution water without addition of the sample to serve as blanks. The DO concentration of one of the bottles of sample dilution was measured using oxygen meter. The same was done to a single blank within 15 minutes of its preparation. The BOD bottles were water-sealed using stoppers and then stored in an incubator for five (5) days at a temperature of 20 °C. Dissolved oxygen concentrations of the incubated samples were then measured at the end of the fifth day and recorded, using Eq. (1):

$$BOD_5 = \frac{\left(D_1 - D_2\right)}{P} \tag{1}$$

Where: BOD₅ is the biochemical oxygen demand after five days, mg/L, D_1 the dissolved oxygen of

the sample which was diluted (15 minutes within preparation), D_2 the dissolved oxygen of diluted sample after incubation and P the decimal fraction of sample used (1/dilution factor)

d. Determination of Chemical Oxygen Demand

One gram of mercuric sulphate was placed into a reflux flask and 10mL of the sample added. 10 mL of N/8 potassium dichromate was added to the flask followed by 20mL of concentrated H_2SO_4 . To act as a blank, another flask was made with 10mL distilled water instead of the sample. The external area of the flask was cooled under running water and 1mL of silver sulphate solution added. Boiling chips were

added to each flask after which the flask was fixed to the condenser. The heaters were switched on and refluxed for about 2 hours at 150°C. This was then permitted to cool and the condenser was washed down with distilled water. The flask was removed and 45mL of purified water was added to each one for dilution. This was cooled under running water to about room temperature. 2 drops of Ferroin indicator was then added. A light blue green colour appeared. The remaining dichromate was titrated using N/8 Ferrous sulphate until it reached a reddish brown end point. The same procedure was used for the blank sample. COD is measured using Eq. (2)

$$COD = \frac{0.1 \times 8000(B_t - S_t)}{V_s}$$
⁽²⁾

Where COD is the chemical oxygen demand, mg/L, B_t the blank titration, and S_t the sample titration

e. Total Heterotrophic Bacteria Count

Nutrient agar media of 28g was dissolved in 1litre of distilled water for 15 minutes; the media was sterilized at 121°C and 15Pascal in an autoclave, and then left to cool to 47°C. The media was put into sterile Petri plates, set aside to solidify, and then dehydrated for 5 minutes in hot air oven set to 40°C. The wastewater samples were inoculated in duplicates using spread plate method and incubated at 37°C for 24 hours. A colony counter was used to count the colonies in the plate, and standard equations were used to count the total heterotrophic bacteria.

f. Total Fungi Count

Sabouraud dextrose Agar media of 65g was dissolved in 1litre of distilled water for 15 minutes, the media was sterilized at 121°C and 15Pascal in an autoclave, then cooled to 47°C. The media was poured into sterilized Petri dishes. After allowing the poured medium to harden, it was dried for 5 minutes in a hot air oven at 40°C. The samples were inoculated in duplicates using spread plate method and incubated at 20°C for 48 hours. A colony counter was used to count the colonies in the plate, and the total fungi were recorded using standard formulae and represented as cfu/ml.

g. Heavy Metals Measurement

Standard solution of the metal of interest was prepared, and then waste water sample was filtered and acidified with 1.5mL concentrated HNO₃ to a pH less than 2 and thereafter divided into 10. The instrument was checked for proper fitting of all tubings, the hollow cathode and deuterium lamp. The standard parameter values (lamp current %, wavelength, slit width, and burner height) for metals to be analyzed were entered correctly, and then the hollow cathode lamp and the deuterium lamp were switched on. The reagents/materials were entered in this sequence: calibration blank (distilled water), standard solutions, stock standard, water samples, spiked sample, stock standard and blank. These steps were repeated for all heavy metals and results were calculated automatically in mg/L. After one heavy metal analysis, auto-zero was entered preceding the next metal.

2.2 Wastewater Samples Treatment

2.2.1 Materials

The materials used for the wastewater treatment includes: very fine sand, fine sand, coarse aggregates, polyurethane membrane, column, aerator pumps, aerator tubes, erlenmeyer flasks, hypochlorite solution, potassium hydroxide (KOH) buffer and magnetic stirrer.

2.2.2 Treatment

The treatment process was carried out in three distinct phases: filtration, aeration and disinfection. Filtration

Trickling filters were designed using polyurethane membrane, and strata of sand beds of variable grain sizes (very fine sand, fine sand and coarse sand in a bottom to top arrangement) overlaid the membrane. The wastewater samples under treatment were made to pass through a column pack of the trickling filters and the filtrates were collected through downward delivery.

Aeration

The filtrates from the filtration unit were oxygenated by bubbling air through them using aerator stones connected to aerator pumps. This process was allowed for 6 hours. This is to provide enough oxygen for stabilization and treatment of the wastewater as oxygen is needed by the bacteria for biodegradation to occur.

Disinfection

A 30ml volume of the aerated filtrate was disinfected with 0.1ml of 11% chlorine solution and vortexed using magnetic agitator then a 0.5ml aliquot of potassium hydroxide buffer was added. This treatment was allowed for 24 hours before a post-treatment analysis was carried out. The treated wastewater samples for analyses were first dechlorinated using sodium thiosulphate

2.3 Estimation of Extent of Treatment of the Wastewater Samples

The extent of treatment (treatment efficiency) is the proportion of pollutant removal (or decrease) in the wastewater samples. It is estimated using Eq. 3 below

Extent of treatment (%)
$$= \frac{P_1 - P_2}{P_1} X 100$$
 (3)

Where P_1 = Concentration of pollutant in the raw waste water sample

 P_2 = Concentration of pollutant in the treated wastewater sample

3. Result

The analytical results of wastewater (raw and treated) from the pulping and bleaching operations from a bamboo based tissue making plant is presented in Table 1 below:

Parameters		Units	Pulping			Bleaching			Regulatory	
						C .			Standard	
			Raw	Treate	Extent of	Raw	Treate	Extent of	FMEn	NESRE
			(P1)	d	Treatmen	(B1)	d	Treatmen	v	Α
				(P2)	t		(B2)	t		
					(%)			(%)		
Ph			7.42	8.08	-8.894	4.49	7.88	-75.50	6-9	6-9
EC		µS/cm	316	4.00	98.73	47.0	4.00	91.49	4000	NS
TDS		mg/l	158	2.00	98.73	24.0	2.00	91.66	2000	500
Turbidity NTU		19.3	9.6	76.17	28.7	5.1	82.22	NS	5.0	
Temper	rature	°C	28.47	28.43	0.140	28.48	28.44	0.140	<40	40
DO			3.66	4.34	-18.58	1.93	4.17	-116.1	Not <2	NS
BOD		mg/l	74.02	4.06	94.51	62.00	4.11	93.37	30-50	30-50
COD			140.3	14.20	89.88	120.4	12.80	89.37	60-90	60-90
			0			0				
TOC		%	10.3	0.1	66.66	7.1	0.1	98.59	NS	NS
	Mercur		< 0.00	< 0.001	0	< 0.00	< 0.001	0	0.05	NS
	У		1			1				
Heav	Lead		0.281	0.040	58.76	0.273	0.041	84.98	<1.00	0.05
у	Nickel	mg/l	0.115	0.003	97.39	0.117	0.008	93.16	<1.00	0.05
Metal	Cobalt		0.193	0.011	94.30	0.208	0.015	92.78	0.5	NS
s	Arsenic		< 0.00	< 0.001	0	< 0.00	< 0.001	0	0.1	NS
			1			1				
THB										
		Cfu/m	1.60 x	0	$10 \ge 10^3$	7.40 x	0	10 x10 ⁹	NS	NS
		1	10 ³			10 ⁴				
Total Fungi		Cfu/m	0	0	0	2.30 x	0	10 x 10 ⁷	NS	NS
		1				10^{3}				

Table 1. Physiochemical Characteristics of Raw and Treated Wastewater

Note. FMEnv (Federal Ministry of Environment), NESREA (National Environmental Standards and Regulations Enforcement Agency), NS (Not Stated), P1 (Raw wastewater from Pulping), P2 (Treated wastewater from Pulping), B1 (Raw wastewater from Bleaching), B2 (Treated wastewater from Bleaching).

3.2 Discussions

The guidelines stipulated by the Federal Ministry of Environment (FMEnv) and National Environmental Standards and Regulations Enforcement Agency (NESREA) were used to evaluate the quality of the wastewater emanating from the pulping and bleaching processes of tissue paper production. The physicochemical results used in this article are values obtained from means of triplicate analysis.

pН

pH is the logarithm of the reciprocal of the hydrogen ion activity present in a given solution, a measure of the activity of free hydrogen (H^+) and hydroxyl (OH) in a solution. For organic compounds and heavy metals removal, the pH of wastewater during treatment is crucial. Alkaline pH favours the precipitation of most metals as insoluble solids (Edokpayi et al., 2015) and plays a major role in determining both the qualitative and quantitative abundance of microorganisms in the wastewater.

The caustic soda (Naoh) used in the pulping process is strongly irritating, corrosive and used mainly for two reasons; Ph control and pulping. The caustic soda is used to keep the pH as close to 8.0 as possible (sodium hypochlorite most effective pH). The pH values recorded for the two raw wastewater samples were 7.42 and 4.49 for the raw wastewater from the pulping and bleaching processes respectively, relative to the range of 6.0-9.0 set by NESREA and FMEnv. The corresponding pH values for the treated wastewater samples from the two processes were 8.08 for the pulping and 7.88 for bleaching processes respectively. This is in accordance with the regulatory body's permissible standard (6.0 - 9.0) for wastewater discharge. This result also corroborates 6.92-8.18 reported by Rout, (2015). The pH values was also in line with the works of Arasappan and Kalyanaraman (2015) and Eremektar et al. (2007) but were greater than that reported by Oluseyi et al. (2019).

Electrical Conductivity (EC)

Electrical Conductivity (EC) is the measure of a solution's ability to conduct electric current which is greatly dependent on the availability of ionic species (Julian et al., 2018). EC is directly proportional to TDS. The conductivity of water is greatly affected by inorganic ions. High EC readings indicate a high concentration of inorganic ions in the wastewater, and. This implies that the ability of an electric current to pass through the wastewater is proportional to the concentration of ionic solutes dissolved in the wastewater (Uwidia & Ukulu, 2013).

Table 1 shows that EC content in the wastewater were 316μ S/cm and 47μ S/cm for the pulping and bleaching units respectively. The result indicates higher EC value in the bleaching process. The result is lower than the range of $435.4 - 576.8\mu$ S/cm reported by Kaur et al. (2010) but within the permissible limit set by FMEnv. The EC of the treated wastewater from both the pulping and bleaching processes were 4.0μ S/cm. The untreated wastewater samples showed higher levels of EC than the treated samples but both the treated and untreated wastewater samples have conductivity values within the FMEnv regulatory limits. The results obtained are similar to those reported by Arasappan and Kalyanaraman (2015) and Mohammed et al. (2017).

Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) is a measure of all dissolved substances in water. Lower TDS indicates better water quality (Uwidia & Ukulu, 2013). It's a metric for the quantity of inorganic salts, organic and other dissolved substances are in water. High concentration of TDS can result in dehydration of aquatic animals (Rachna & Disha 2016). The Total Dissolved Solids (TDS) for the raw wastewater samples from the pulping and bleaching processes were 158mg/l and 24mg/l respectively. The increase in the amount of TDS in the pulping process wastewater sample could be as a result of the presence of dissolved ions of organic and inorganic solvents, the residues of caustic soda and ammonia, nitrates, hydrogen, nitrogen, calcium, sodium and other dissolved salts (Kannan et al., 2009).

The treated samples levels were 2mg/l each for the samples indicating a significant reduction in the TDS content. These values are within the FMEnv, and NESREA permissible limits of 2000mg/l and 500mg/l respectively. Thus, the wastewater samples' TDS for the untreated and treated samples conformed to the threshold regulatory standards. Furthermore, the findings of this study coincide with Mohammed et al., 2017 but less than of 4354 – 5768mg/l and 2002 – 7463mg/l reported by Kaur et al. (2010) and Ghaly et al. (2011) respectively.

Turbidity

Turbidity is a water quality term that refers to the relative clarity of water. It can also be described as the opaqueness of a fluid due to the presence of suspended solids that reduces the passage of light through the water. This is an indicator that high number of particles or sediments are suspended (or dissolved) in the water and therefore, water with low turbidity is clearer.

The turbidity values recorded for the raw waste water samples were 19.3NTU and 28.7NTU for the pulping and bleaching processes respectively. These figures were greater than the regulatory body's requirements. Wastewater with turbidity of 5NTU is visibly cloudy while at 25NTU, water becomes murky. The high turbidity of the raw wastewater samples could be attributed to organic and inorganic matter, microscopic organisms, bamboo ashes, bamboo chips etc.

The turbidity levels of the treated samples were 9.6NTU and 5.1NTU for the pulping and bleaching processes respectively. The values obtained after treatment of the pulping wastewater sample was higher than the permissible level (9.6 as against 5.0NTU) while that from the bleaching process was 5.1 NTU. The turbidity reduction in this study agrees with the work of Karthik et al. (2011) on effluent turbidity removal. This value of turbidity could be attributed to black liquor used in soda pulping, bamboo colour and a great variety of suspended solids.

Temperature

Temperature is a physical quantity that expresses hotness or coldness. The temperature difference between the raw wastewater samples from the pulping and bleaching processes and the treated wastewater samples were insignificant. The temperature of the raw wastewater from the pulping process was 28.47°C while that of bleaching process was 28.48°C. The corresponding treated wastewater samples' temperature were 28.43°C and 28.44°C for the pulping and bleaching units

respectively and may be due to the heat generated by the mixture of caustic soda, ammonia and steam used in the digester. These results are similar to the temperatures of wastewater reported by Akan et al. (2007).

The temperature range of 28.43°C - 28.48°C for both the treated and untreated samples were within the FMEnv and NESREA permissible limit for wastewater discharge (<40°C), thus these wastewater cannot be associated with thermal pollution (Bhatia, 2005).

Dissolved Oxygen

Dissolved Oxygen (DO) is the amount of oxygen that is dissolved in water and is necessary for survival of aquatic life. It also serves as a crucial indication of ecological health. DO levels in water are partly dependent on the chemical, physical and biochemical activities taking place in the water (Julian et al., 2018).

The DO levels of raw wastewater from the pulping and bleaching processes were 3.66mg/l and 1.93mg/l respectively. The treatment of the wastewater increased the DO levels to 4.34mg/l and 4.17mg/l for the wastewater from the pulping and bleaching operations. The low DO concentration in the raw wastewater samples is an indication of high microbial activities in the water due to the presence of biodegradable organic compounds like cellulose and suspended matter (Bhatia, 2005).

In addition, the values for DO in the treated and the untreated wastewater samples from pulping operation are lower than the saturation value (7.5mg/l) at 30°C (Hubbe et al., 2016) but within regulatory standards. However, the untreated wastewater sample from the bleaching process as shown in Table 1 is below FMEnv regulatory standards (Not <2mg/l). This mandates treatment of wastewater before discharge. This study's outcome is higher than those reported by Mohammed et al. (2017) and Akan et al. (2007) and maybe due to differences in the industries assessed.

Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD) is the amount of dissolved oxygen needed by aerobic biological organisms to breakdown organic materials present in water. The quantity of BOD in water has a significant impact on DO. Discharge of wastewater containing high levels of BOD into surface water body can result in dissolved oxygen depletion and subsequently, the death of aquatic species in the recipient water body, i.e., the higher the BO concentration, the greater the extent of oxygen depletion in the water bodies (Rachna & Disha, 2016).

The BO values recorded were 74.02mg/l and 62.00mg/l for the samples of the raw wastewater from the pulping and bleaching operations respectively while the corresponding levels of BOD_5 for the treated samples were 4.06mg/ and 4.11mg/l. The result showed that wastewater from pulping operations are more polluted than those from bleaching operations which could be linked to the heterogeneous mixture of various organic compounds and multiple reagents employed in the bleaching process (FEPA, 1999).

The BOD level of the wastewater from bleaching operation (62.00mg/l) and that of the pulping operation (74.02mg/l) were higher than the FMEnv and NESREA permissible standard of 30-50mg/l.

However, the values recorded after treatment from the two operations were within the various regulatory values, and also in compliance with standards for the pulp and paper industry for wash waters from pulping and bleaching processes and spent black liquor of 15mg/l hence, the treated samples can be discharged into the environment. This implies that industrial wastewater treatment is sacrosanct. The values of these finding is below that obtained by Noorjahan, 2014 (600-1622 mg/l).

Chemical Oxygen Demand

The Chemical Oxygen Demand (COD) is the amount of oxygen consumed to chemically oxidize organic water contaminants to inorganic end products. It's also the oxygen equivalent of the sample's organic content that's vulnerable to oxidation by a strong chemical oxidant. It is usually higher than BOD because some organic materials in the water that are resistant to microbial oxidation and hence, not involved in BOD₅ could be chemically oxidized.

The COD of the raw wastewater generated from the pulping and bleaching processes were 140.30mg/l and 120.40mg/l respectively. This could be due to the concentration of increased organic matter and decaying plant. It also indicates the presence of high level of biodegradable compounds. The results obtained after treatment were 14.20mg/l and 12.80mg/l. The resulting COD values were within limits (60 - 90 mg/l) for wastewater discharge stipulated by the regulatory bodies (FMEnv and NESREA) and also in compliance with standards for the pulp and paper industry for wash waters (100mg/l). The values obtained are similar to the result noted by Edokpayi et al., (2017).

Total Organic Carbon

The Total Organic Carbon (TOC) concentration in a sample indicates the availability of carbonaceous organic matter in that sample (wastewater, soil and sediment organic matter) (Gonder et al., 2011). Several studies have also used TOC to explain the carbon cycle system and the conversion of organic carbon into carbon dioxide which plays a vital role in atmospheric change often caused by global warming (Aiken et al., 2002).

The concentration of TOC in the raw wastewater from the pulping unit was 10.3%. This high value of TOC could be because bamboo is an organic material while that of the bleaching process is 7.1%. The corresponding values for the two treated wastewater samples were 0.1% each. This shows a very high efficiency of treatment.

Heavy metals

Heavy metals are natural components of the Earth's crust. The term "heavy metal" is collectively applied to a collection of metal and metal-like elements with a density greater than 5g/cm3 compared to water and atomic number above 20. They are potentially toxic trace elements and their impacts maybe felt in organisms at low concentrations. Heavy metals such as Mercury, Arsenic, Cobalt, Nickel, Zinc, Chromium, Lead etc. are toxic at high concentrations and are detrimental to living organisms because degradation becomes impossible (Williams & Dimbu, 2015).

Mercury

Mercury (Hg) known as quick silver is a chemical element used mostly in pressure measuring devices

and also a good conductor of electricity. It is the only metal that is a liquid at standard temperature and pressure (Williams & Dimbu, 2015). The values of mercury recorded for both the raw waste water samples and the treated waste water samples from the pulping and bleaching processes were<0.001 across the two stages and within 0.05mg/l of FMEnv. It therefore poses no threat to the recipient environment.

Lead

Lead (Pb) is a heavy, soft, malleable, bluish grey metal and is a famous highly toxic metal measured as a priority pollutant. It's an industrial pollutant that makes its way into the ecosystem via soil, air, and water. It is seen as a systematic poison causing anemia, kidney malfunction, brain tissue damage of brain and death (Singha, 2012). The Maximum Permissible Limit (MPL) of lead in wastewater is <1.00 for FMEnv and 0.05mg/l of NESREA. The results derived from this study are 0.281mg/l and 0.273mg/l for the raw wastewater from pulping and bleaching processes while the treated samples were 0.040mg/l for the wastewater from pulping and 0.041mg/l for the wastewater from bleaching respectively. The lead contents in the raw wastewater from the pulping and bleaching operations were below the values stipulated by NESREA and can be released into the ecosystem but treatment of the wastewater samples are highly recommended in order to reduce the quantity of Pb to the barest minimum.

Nickel

Nickel (Ni) is a silver-colored metal utilized in making stainless steel, electronics and coins among other uses (Group, 2013). Globally, the release of Nickel to the environment is predicted to vary from 150,000 to 180,000 metric tons per year (Kacprzak et al., 2003). Nickel levels in the raw wastewater from the pulping and bleaching processes were 0.115mg/l and 0.117mg/l respectively. The values of Nickel in the treated samples were 0.003mg/l and 0.008mg/l for pulping and bleaching respectively. The resultant values are within acceptable standard requirement for discharge.

Cobalt

Cobalt (Co) is also a very toxic element disturbing the environment and highly present in industrial wastewater. Heavy metals like cobalt are toxic because of their solubility in water and its high accumulation may not only result in soil contamination but affect food quality and safety (Mohsen & Seilsepour, 2008). The cobalt values recorded for the wastewater sample from pulping was 0.193mg/l and 0.208mg/l for that of bleaching. This result is lower than that of Oladeji and Saeed, 2015 and within the value recommended by the FMEnv. The concentrations in the treated samples were 0.011mg/l for pulping and 0.015mg/l for bleaching. There was diminution in the Cobalt value after treatment, and conforms to the 0.5mg/l limit by the FMEnv.

Arsenic

Arsenic, a metalloid occurring naturally as a component of the Earth's crust, is toxic to humans and the environment occurs in many minerals, usually mixed with sulfur and other metals but also as a pure elemental crystal. High arsenic level in wastewater is mainly arsenic containing waste acid which might be resulting from circulating cooling water, acidic heavy metal, wastewater, etc., the FMEnv

gives a limit of 0.1mg/l. the results of the analysis is <0.001 across the raw wastewater samples from pulping and bleaching operations and the corresponding treated wastewater samples from these two processes. The results as shown corresponds with the safe limits stipulated by the regulatory bodies and are not toxic to human and aquatic life.

The results obtained for all heavy metals in the wastewater samples after the treatment are within permissible limit and are similar to results achieved in the research carried out by Kinuthia et al., 2020 in Lagos State, Nigeria.

Microbiological Components

Total Heterotrophic Bacteria includes all bacteria that use organic nutrients for growth. These bacteria are universally present in all water types, food, air and soil. For these bacteria to pose health risks, it is must be present in an infectious dose i.e. sufficient concentration. Fungi, on the other hand are a group of spore-producing organisms feeding on organic matter. Most fungi are saprophytic and not pathogenic to plants, animals and humans although a few fungal species are phyto-pathogenic and cause disease in man, producing toxins that affect the ecosystem.

The total heterotrophic bacteria level of the raw wastewater from the pulping process is 1.60×10^5 cfu/ml while the resulting value from the bleaching process is 7.40×10^4 cfu/ml which is higher for the wastewater. The total fungi recorded for the raw wastewater sample from pulping was 0cfu/ml whereas 2.30×10^3 cfu/ml was recorded for that from bleaching. Going by NESREA standard $(1 \times 10^2$ cfu/ml), any water contaminated to this extent or level is not supposed to be released into the environment directly without treatment. The values are as a result of abundance of microorganisms which are present in the wastewater and in which microbes throve (Neboh et al., 2013). Rabah et al. (2008) reported a similar finding of 7.30×10^7 cfu/ml, Adesemoye et al., 2006 reported total heterotrophic bacteria of 3.32×10^7 cfu/ml and total fungi of 1.60×10^5 cfu/ml. Ogbonna and Igbenije, 2006 reported a mean total heterotrophic bacterial population of 2.08×10^2 cfu/ml and a total fungi population of 8.0×10^2 cfu/ml respectively from wastewater collection sites in Port Harcourt City, Rivers State, Nigeria.

The total heterotrophic bacteria and total fungi for both the treated and untreated wastewater samples from the tissue paper production operation's pulping and bleaching operations were recorded as 0. This demonstrated that the wastewater treatment efficiency was 100 percent and that it was safe to discharge into the environment.

4. Conclusion

The study assessed the pollution loads of wastewater from the pulping and bleaching units of the tissue paper making industry. It also treated, characterized and evaluated the extent of treatment of the wastewater. The composition of the two raw wastewater samples showed that the waste water from the bleaching section was more polluted than those from the pulping unit. The treatment carried out on the wastewater samples showed high level of efficiency evident in the reduction of the pollutants in both samples. The average extent of treatment was slightly above 70% for the sample from the pulping unit

and about 80% for that from the bleaching unit. The result after treatment showed that all the parameters except turbidity were within regulatory limit. This could be linked to the virgin fibre from bamboo used compared to other similar industries that uses waste papers from different sources.

The pollutant levels in the treated samples were in compliance with those of the regulatory agencies (FMEnv and NESREA), hence, if the proposed treatment scheme is adopted, the wastewater will be accepted for discharge into the environment.

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