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Research Article

Evaluation of Discharged Untreated Wastewater from Pulping and Bleaching Operations in a Bamboo Based Tissue Paper Making Plant in Nigeria

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Abstract:
This study on Evaluation of Discharged Untreated Wastewater from Pulping and Bleaching operations in a Bamboo Based tissue Paper Making Plant in Nigeria was conducted mainly to evaluate the pollutant loads present in wastewater produced during the Pulping and Bleaching operations of the tissue paper making progression. The wastewater samples were obtained and examined to find out the pollutants they contain by checking the availability of some physicochemical parameters using standard methods by American Public Health Association (APHA). The analyzed parameters obtained for the pulping and bleaching processes respectively are pH (7.42 and 4.49), EC (316µS/cm and 47µS/cm), TDS (158mg/l and 24mg/l), Turbidity (19.3NTU and 28.7NTU), Temperature (28.47°C and 28.48°C), DO (3.66mg/l and 1.93mg/l), BOD_5 (74.02mg/l and 62.00mg/l), COD (140.30mg/l and 120.40mg/l), TOC (10.3% and 7.1%), THB ($1.60x10^3$cfu/ml and $7.40x10^4$cfu/ml), THF (0cfu/ml and $2.30x10^3$cfu/ml) and heavy metals like Hg (<0.001mg/l and <0.001mg/l), Pb (0.281mg/l and 0.273mg/l), Ni (0.115mg/l and 0.117mg/l), Co (0.193mg/l and 0.208mg/l) and As (<0.001mg/l and <0.001mg/l). These results were also compared amid the permissible regulatory standards set by the FMEnv and NESREA. From the comparative analysis, the bleaching wastewater sample was more polluted than that from pulping. EC, TDS, BOD_5, COD, TOC and Pb were higher in the pulping wastewater sample which could be attributed to the organic nature of the starting material; bamboo and residues of the pulping agents; caustic soda and ammonia while Acidity, Turbidity, Temperature, DO, Ni, Co, THB and TF were higher in the bleaching wastewater sample and could be caused by the bleaching agents and the availability of microorganisms. The result showed that some parameters except BOD_5, turbidity, COD, DO and pH from pulping fell within regulatory limit. This could be linked to the virgin fibre from bamboo applied which contains less pollutant compared to other industries using waste papers from different sources.

Keywords: Bamboo, Fibres, Wastewater, Pulping, Bleaching, Tissue Paper

Introduction

Wastewater includes effluents from industries, fertilizer, pesticide solutions, landfill leachates, urban overflow of toxic wastewater, garbage, mining wastes, fats, oils or grease (FOG), oil, sludges and unsafe household liquids. These liquids are generally dangerous with propensity to harm humans and the environment. They are mostly by-products of manufacturing operations or discarded commercial products (Elhaj, 1984).

Tissue paper, often known as tissue, is a thin, lightweight paper created from recycled pulp or pulped wood. (Nanko et al, 2005). "Tissue" comprises of all paper materials used for hygienic purposes both in private residence and in public places. Tissue is toilet paper, kitchen towels, handkerchiefs, napkins, facial tissues, therapeutic sheets, etc. Papers in this category are soft, feathery, light, and highly. They are also absorbent, rip resistant, disposable, and moderately sturdy (Kilby and Crevecoeur, 2014). Tissue properties are determined by consumer preferences than by industrial requirements (Novotny, 1988). According to Kan and Wong (2015), the key properties of tissue are absorbency, basis weight, thickness, bulk (specific volume), brightness, perforation efficacy, appearance, softness, comfort and wet Strength.

Tissue paper is produced using a variety of fiber types, classified based on their source: virgin fibers (fibers from wood pulping) and recycled fibers (fibers from re-pulping used paper) (FisherSolve, 2017). The virgin fibers could be from diverse hardwoods (aspen, maples, birches, beech, oaks, poplar, ash, beech, and eucalyptus camaldulensis), softwoods (Pines, hemlocks, firs, larches, spruces, cedar), and non-woody fibres (bamboo, wheat straw, bagasse, sisal, abaca, flax, hemp, kenaf, flax bagasse, maize stalks, sorghum stalks) (Zou and Liu, 2016).

Bamboo is an eco-friendly option for making products. It is highly renewable as it grows quickly, occupies little land, and requires no fertilizers or insect repellents to thrive, hence, the edge in environmental friendliness. It is a biomass, characterized by long and semi-long fibers similar to hard and soft woods (Lewis and Carol, 2008), has a higher fines percentage, higher 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 and produces 30% more oxygen (Phillips et al., 2015). It has natural antibacterial properties while the decomposing discarded leaves provide nutrients needed for growth. The nature of bamboo employed for making tissue is the dry Bamboo (Moso Phyllostachysedulis) which is a temperate species of gigantic timber bamboo, indigenous to China and Taiwan with global spread (Wang and Kong, 2011). This bamboo specie grows to 28 m (92 ft) in height and spreads by both asexual and sexual reproduction method with asexual reproduction being the most common (Lewis and Carol, 2008). Its ability to grow so quickly makes it replenished immediately after utilization and so, causes no deforestation. It forms part of a majority of efficient and environmentally friendly materials available. Bamboo goods have a lesser environmental impact and may be maintained to minimize overconsumption owing to their adaptability and renewability. Despite being a grass, bamboo possess related features to hardwoods e.g. oak, maple or birch, which are commonly mixed with softwood trees like pine to make tissue paper and due to its tendencies of being transformed into soft goods (tissue, clothes), and other robust items (roads, buildings, furniture, etc.).

The production of tissue paper from bamboo requires high energy, virgin fiber pulp and water (Paulapuro, 2000). The paper industry which also produces tissue is ranked sixth largest polluter that discharges particulates, liquid and solid wastes into our surroundings (Ugurlu et al., 2008). Major pollution sources from this industry include pulping, washing and bleaching processes. These processes utilize enormous volumes of water that resurface in the form of environmentally damaging effluents (Kamil et al., 2011). The effluents from the process have several amounts of hazardous chemical contents that may have negative environmental consequences if released directly into the environment. (Ghaly et al., 2011). This paper processing wastewater, containing toxic and intensely coloured organic substances is portrayed by a high intensity of Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD_5) and other physicochemical parameters (Wang and Kong, 2011). These parameters are of concern, particularly given the increased desire for tissue paper and other paper products.

Bamboo pulp is typically prepared from Moso *bamboo (*phyllostachyspubescens) by soda or sulfate digestion process. The unbleached pulp is employed in package paper production, whereas the bleached bamboo pulp is utilized in producing offset paper, tissue paper, typing/printing paper, and first grade culture paper. Bamboo is an excellent material for papermaking due to its long fiber and similar characteristics to softwood (Philips et al., 2015). It has a higher tearing strength and evenness than hardwood pulp which makes the demand for bamboo pulp to grow. Bamboo pulp is inexpensive compared to other wood pulps. (Nanko et al., 2005).

Bamboo is an excellent tissue paper material because the products are soft, sturdy and very renewable. Bamboo tissue paper is an alternative to regular wood or fibre pulp tissue paper because it is more sustainable (Zou and Liu, 2016). Comparing with toilet paper made from recycled and other virgin pulps, bamboo tissue paper is rated higher. However, bamboo tissue paper and virgin toilet paper are equal in softness. It is both soft and thick, which makes it give the most comfort and all the needed absorbency. The process of tissue paper making is presented in Figure 1.

Materials and Methods

Tissue Paper Production Process

The main raw material employed in tissue paper manufacturing in this article is dry bamboo; Moso bamboo (Phyllostachysedulis). The bamboo is cut into sizes of 10 – 25mm and crushed into tiny fine particles by the crushing machine and then conveyed into the digester for pulping. The digester contains a solution of water, ammonia and caustic soda. A variety of chemicals are put into the system at different stages to enable the finished tissue paper have unique features like strength, brightness, softness, shade and thickness. The pulp is allowed to ferment 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 pulp in water previously treated with industrial salt. Also, steam is applied to rapidly transport fine fibres to the mixer (production pool). A lot of wastewater is produced containing a combination of caustic soda and ammonia (black liquor) that are thereafter discharged into the environment. The wastewater is generally from the various washing operations at different stages of production.

Black fibres are washed by chemicals introduced into the digester until the water becomes clean and white, but the fibres remain black. The pulp fibers are vibrated and passed through a vibrating screen, which allows only fine fibers to pass through while charfs and other 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 remainder is discarded and the fibers are transported to the bleaching section where hypochlorite is added to whiten the fibers. Pulp bleaching is done to advance the whiteness of 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 into 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). Part of the water is removed by drying on steam heated cylinders with felts which generates the steam that is sent into the pool.

The produced tissue is then peeled away from the mother rolls with a knife and wrap into a jumbo reel in a cone. The rewinder machine receives the master or jumbo reels. The rolls are then cut to the proper sizes, samples are gathered and examined for quality control compliance, and the product is subsequently packaged for sale.

Flow Chart for Tissue Paper Making from Bamboo

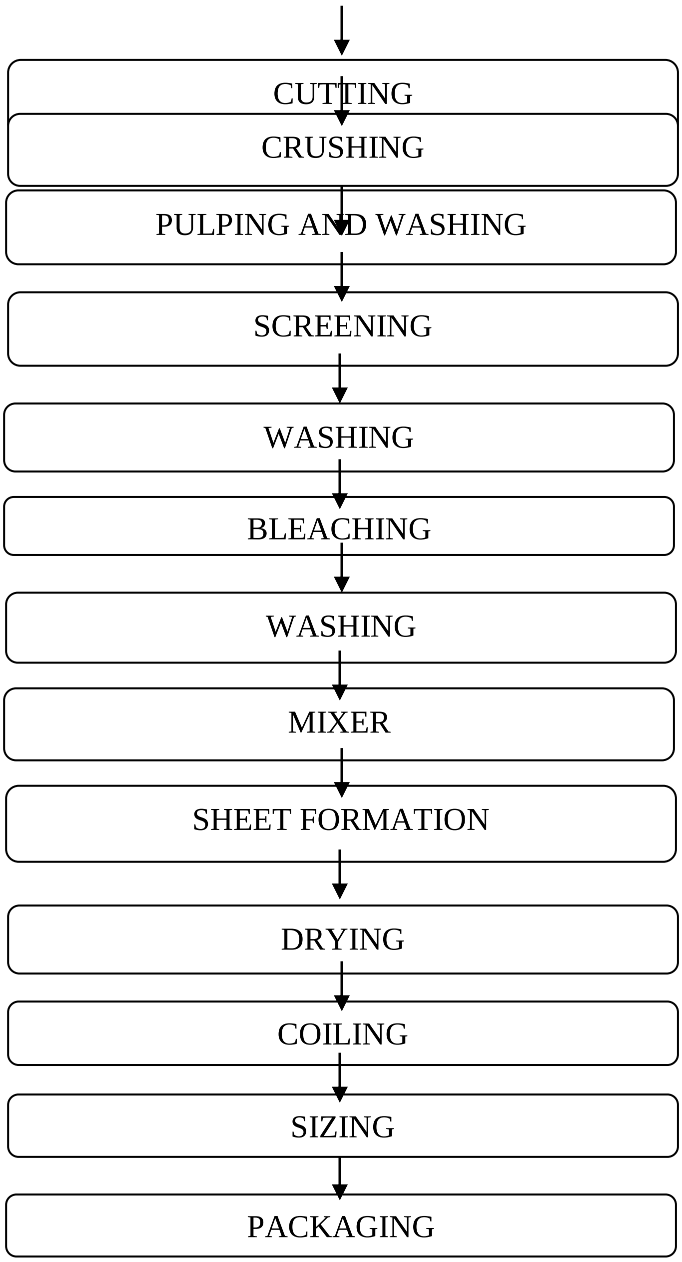

Fig 1 Processes of Tissue Paper Production

Wastewater Collection and Handling

Two wastewater samples from the bamboo based tissue paper factory were collected with the aid of 1000ml glass bottles, properly labelled, stored in icepack, transported to the laboratory and analyzed. These wastewater were produced 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.

Methods

The following equipment/apparatus were employed in the analysis. They includes: 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.

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 pulping and bleaching 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 harmony with APHA 2130B (APHA, 2012). The meter was calibrated with formazin standard solution of 20, 100 and 800 Nephelometric transfer unit, NTU, from HACH. For measurement, 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 meticulously 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 kept 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 fifth day ending and recorded, using Eq. (1):

$$BOD_5 = \frac{(D_1 - D_2)}{P} \quad (1)$$

Where: BOD_5 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 which was thereafter fixed to the condenser. The heaters were switched on and refluxed for about 2 hours at 150^oC. 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)

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

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 HNO_3 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.

Results and Discussion

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

TABLE1: Pulping and Bleaching Wastewater Characteristics

Parameters		Units	Untreated Wastewater		Regulatory Permissible Standard	
			Pulping	Bleaching	FMEnv	NESREA
Ph			7.42	4.49	6-9	6-9
Electrical Conductivity		µS/cm	316	47.0	4000	NS
Total Dissolved Solids		mg/l	158	24.0	2000	500
Turbidity		NTU	19.3	28.7	NS	5.0
Temperature		°C	28.47	28.48	<40	40
Dissolved Oxygen			3.66	1.93	Not <2	NS
BOD_5		mg/l	74.02	62.00	30-50	30-50
COD			140.30	120.40	60-90	60-90
TOC		%	10.3	7.1	NS	NS
Heavy Metals	Mercury	mg/l	<0.001	<0.001	0.05	NS
	Lead		0.281	0.273	<1.00	0.05
	Nickel		0.115	0.117	<1.00	0.05
	Cobalt		0.193	0.208	0.5	NS
	Arsenic		<0.001	<0.001	0.1	NS
Total Heterotrophic Bacteria		Cfu/ml	1.60 x 10	7.40 x 10^4	NS	NS
Total Fungi		Cfu/ml	0	2.30 x 10^3	NS	NS

NOTE: FMEnv = Federal Ministry of Environment, NESREA= National Environmental Standards and Regulations Enforcement Agency, NS (Not Stated),

Discussion of Results

The values of physicochemical parameters tabulated in Table 1 above are means of triplicate testing.

pH

pH, the logarithm of the reciprocal of the hydrogen ion activity present in a given solution, measured in a scale of 0 to 14, is a measure of the activity of free hydrogen (H^+) and hydroxyl (OH^-) in a solution. It is an indicator of the acidic and alkaline conditions of the wastewater samples. The caustic soda (Naoh) employed during pulping is strongly irritating and corrosive and it's used mainly for two reasons; for pH control and for pulping. The essence of the caustic soda is to keep the pH as close to 8.0 as possible because sodium hypochlorite is most effective at that pH that is why the pH value after pulping is 7.42. For the elimination of organic compounds and heavy metals, 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 pH values recorded for the two raw waste water samples were 7.42 and 4.49 for the untreated waste water from the pulping and bleaching processes respectively. The results showed that wastewater from the pulping process was slightly alkaline (7.42) and within regulatory standards while the untreated wastewater from the bleaching process was highly acidic (4.49). The latter could be associated with the high acid content of the bleaching agents.
The pH values obtained corroborated the works of Eremektar et al., (2007) and, Arasappan and Kalyanaraman, (2015) but were greater than that reported by Oluseyi et al., (2019).

Electrical Conductivity

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). Water conductivity is greatly affected by inorganic ions. High EC readings indicate a high concentration of inorganic ions in the waste water, and EC directly directly proportional to TDS. This implies that the ability of an electric current to pass through the wastewater is relatively proportional to the concentration of ionic solutes liquefied in the wastewater (Uwidia and Ukulu, 2013).
The EC content in the pulping wastewater sample was 316µS/cm while 47µS/cm was recorded in the wastewater obtained from the bleaching process. The recorded values are less than the range (435.4 – 576.8µS/cm) reported by Kaur et al., (2010) but within FMEnv permissible limit. The conductivity of the wastewater samples from the pulping operation was about seven times the values recorded for that from bleaching operations but still within FMEnv limit. The results obtained are similar to those obtained by Mohammed et al., (2017) and Arasappan and Kalyanaraman, (2015).

Total Dissolved Solids (TDS)

Total Dissolved Solids (TDS) is a measure of all dissolved substances in water (Uwidia and Ukulu, 2013). It is a metric for the quantity of inorganic salts, organic material, and other dissolved materials are in water. The Total Dissolved Solids (TDS) for the untreated 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 potassium plus other dissolved salts (Kannan et al., 2009). High concentration of TDS can result in dehydration of aquatic animals (Rachna and Disha 2016).
These values are however, within the FMEnv and NESREA permissible limits of 2000mg/l and 500mg/l respectively. Thus, the wastewater samples TDS conformed to the threshold regulatory standards. The values recorded also corroborated the findings of Mohammed et al., 2017 but lower than those reported by Kaur et al., (2010).

Turbidity

Turbidity is a water quality term referring to the relative clarity of water. It is also described as the opaqueness of a fluid due to the availability of suspended solids that reduces passage of light through the water. It is measured in NTU (Nephelometric Turbidity Units) and indicates that high number of particles (or sediments) are suspended in or liquefied in the water. Water with low turbidity therefore appears clearer.
The turbidity values recorded for the untreated wastewater samples were 19.3NTU and 28.7NTU for the pulping and bleaching processes respectively. These figures were much greater than the regulatory body's requirements. Wastewater with turbidity of 5NTU is visibly cloudy while at 25NTU, it becomes murky. The high turbidity of the untreated wastewater samples could be linked to the fine organic and inorganic matter, microscopic organisms, bamboo ashes, bamboo chips etc. The turbidity level in this study 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 hot and cold. There were just minimal differences in the temperatures of the untreated wastewater samples from the pulping and bleaching processes. The temperature of the untreated wastewater from the pulping process was 28.47^{o}C while that from the bleaching process was 28.48^{o}C. These results are similar to the temperatures of wastewater reported by Akan et al., 2007 and Odeyemi et al., 2011.
The temperatures of 28.47^{o}C and 28.48^{o}C for both samples were within the FMEnv and NESREA permissible limit for wastewater discharge (<40^{o}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. It is necessary for aquatic life to survive, and so, serves as a crucial indication of ecological health. DO levels in water are partly dependent on the chemical, physical and biochemical activities occurring in the water (Julian et al., 2018) and is influenced by water temperature, movement, salinity etc.
The DO levels of the untreated wastewater from the pulping and bleaching processes were 3.66mg/l and 1.93mg/l respectively. The low DO concentrations in the untreated wastewater samples are indications of high microbial activities in the water due to the

presence of biodegradable organic compounds like cellulose and suspended matter (BritonBi et al., 2006). In addition, the value for dissolved oxygen in the untreated wastewater sample from the pulping operation is higher than regulatory standards but that from the bleaching process is below regulatory standards (FMEnv Not <2mg/l). This mandates treatment of wastewater before discharge. The values recorded in this study are at variance (higher) with those reported by Akan et al., 2007 and Mohammed et al., 2017 and maybe due to differences in the industries assessed.

Biochemical Oxygen Demand

Biochemical Oxygen Demand (BOD_5) is the amount of dissolved oxygen, (DO) needed by aerobic biological organisms to breakdown organic materials present in water. The amount of BOD_5 in water has a significant impact on dissolved oxygen (DO). Discharge of wastewater containing high levels of BOD_5 into water bodies can result in dissolved oxygen depletion and death of aquatic species in the recipient water i.e. the higher the BOD_5 concentration, the greater the extent of oxygen depletion in the water bodies (Rachna and Disha, 2016).

The BOD_5 values recorded were 74.02mg/l and 62.00mg/l for the sampled wastewater from pulping and bleaching operations respectively. The result showed that wastewater from pulping operations are more polluted than those from bleaching operations, and this could be linked to the heterogeneous mixture of various organic compounds and multiple reagents employed in the bleaching process. The BOD_5 content of the wastewater from bleaching operation (62.00mg/l) and that of the pulping operation (74.02mg/l) are higher than the FMEnv and NESREA permissible standard of 30 – 50mg/l and standards for the pulp and paper industry for wash waters from pulping and bleaching processes and spent black liquor of 15mg/l. These values are lower than that reported by Noorjahan, 2014 (600-1622 mg/l).

Chemical Oxygen Demand

Chemical Oxygen Demand (COD) is the amount of oxygen used up chemically to oxidize organic water contaminants to inorganic end products. It is the oxygen equivalent of the sample's organic content that's vulnerable to oxidation by a strong chemical oxidant and is usually higher than the BOD for the reason that some organic substances in the water that are resistant to microbial oxidation and hence, not involved in BOD are easily chemically oxidized (Sulaiman et al., 2016).

The COD of the untreated 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 easily biodegradable compounds. This result is higher than the limit (60 – 90mg/l) for wastewater discharge of stipulated by the regulatory bodies as well as the standards for the pulp and paper industry for wash waters from pulping and bleaching processes and spent black liquor of 100mg/l. The values recorded are comparable to the concentrations noted by Edokpayi et al., 2017.

Total Organic Carbon

The Total Organic Carbon (TOC) in a sample indicates the availability of carbonaceous organic matter in waste water, soil or sediment (Byun et al., 2010). 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 climate change caused by global warming (Aiken et al., 2002).The TOC content of the untreated wastewater from the pulping operation is 10.3% while that of the bleaching process is 7.1%. This high TOC value in the wastewater sample from the pulping unit could be attributed high organic content in bamboo while the reduced value from the bleaching unit could be linked to the presence of dissolved ions of hypochlorite used as a bleaching agent and other organic matter.

Heavy metals

Heavy metals are natural components of the Earth's crust. They are potentially toxic trace elements and their impacts maybe felt in organisms at low concentrations (Adekunle et al., 2012). Heavy metals such as Mercury, Arsenic, Cobalt, Nickel, Zinc, Chromium, Lead etc. are toxic at moderate and high concentrations and therefore detrimental to living organisms because degradation becomes impossible. Leaching of the heavy metals into groundwater also is a primary cause for concern especially because of the recalcitrant nature of the metals (Williams and Dimbu, 2015).

Mercury (Hg)

Mercury 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. The values of mercury in the untreated wastewater samples from the pulping and bleaching processes were<0.001mg/l and were within 0.05mg/l permitted by FMEnv.

Lead (pb)

Lead is a heavy, soft, malleable, bluish grey metal and a famous highly toxic metal measured as a priority pollutant (Mondal, 2009). It is described as an industrial pollutant that makes its way into the ecosystem through soil, air, and water. It has been reported to be a systematic poison causing anemia, kidney malfunction, brain tissue damage and death (Singha, 2012). The maximum permissible limit of lead in wastewater is <1.00 for FMEnv and 0.05mg/l for NESREA. The results obtained from this study are 0.281mg/l and 0.273mg/l for the untreated wastewater from pulping and bleaching processes respectively. The lead contents in the untreated wastewater samples from the two operations (pulping and bleaching) were higher than the values stipulated by the regulatory bodies.

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 (Kasprzak et al. 2003). Nickel levels in the untreated wastewater from the pulping and bleaching processes were 0.115mg/l and 0.117mg/l respectively. The resultant values are within acceptable standard requirement for discharge but does not exclude treatment as treatment will reduce the concentration and also prevent buildup of the metal in the recipient body (soil or water)

Cobalt

Cobalt (Co) is a very toxic element affecting the environment and mostly present in industrial wastewater. Heavy metals like cobalt are deadly because of their solubility in water and high accumulation that result in soil contamination thereby affecting both food quality and safety (Mohsen and Seilsepour, 2008).The cobalt values recorded for the wastewater samples were 0.193mg/l and 0.208mg/l for pulping and bleaching respectively. These values are lower than those reported by Oladeji and Saeed (2015) and are also within the value recommended by the FMEnv.

Arsenic

Arsenic, a metalloid occurring naturally as a component of the Earth's crust, is toxic to humans and the environment. High arsenic level in wastewater is mainly arsenic containing waste acid which might be resulting from circulating cooling water. The concentration of arsenic was <0.001 in the untreated wastewater samples from pulping and bleaching operations and therefore within both FMenv and NESREA threshold limit of 0.1mg/l. The results as shown corresponds with the safe limits stipulated by the regulatory bodies and are not toxic to human and aquatic life.

Microbiological Components

Total Heterotrophic Bacteria includes all bacteria that make use of organic nutrients for their growth. These bacteria are commonly present in all water types, food, air and soil. For these bacteria to create a health risk, it is required to be present in an infectious dose i.e. sufficient concentration. Fungi, on the other hand are group of spore-producing organisms feeding on organic matter. Most fungi are saprophytic and not pathogenic to plants, animals and humans. However, a few fungal species are phyto-pathogenic and cause disease in man and produce pollutants that affect the ecosystem.
The total heterotrophic bacteria of the untreated wastewater from the pulping and bleaching operations were 1.60×10^5cfu/ml and 7.40×10^4cfu/ml respectively. Also, the total fungi count recorded for the untreated wastewater sample from the bleaching process 2.30×10^3cfu/ml. but not detected in the wastewater from the pulping operation. NESREA standard (1×10^2cfu/ml), recommends that any water contaminated to this extent is not appropriate for discharge into the environment directly without treatment. The values could be due to abundance of microorganisms present in the wastewater and in which microbes throve (Neboh et al. 2013). Rabah et al., (2008) noted a similar finding of 7.30×10^7cfu/ml, Adesemoye et al., (2006) reported total heterotrophic bacteria of 3.32×10^7cfu/ml and total fungi of 1.60×10^5cfu/ml while Ogbonna and Igbenije(2006) recorded a mean total heterotrophic bacterial population of 2.08×10^2cfu/ml and a total fungi population of 8.0×10^2cfu/ml respectively from waste water collection sites in Port Harcourt City, Rivers State, Nigeria.

Conclusion

The study compared the pollution loads of wastewater from the pulping and bleaching units of a tissue paper making industry which uses bamboo as its untreated material. The comparative analysis of the composition of the two untreated wastewater samples showed that the wastewater from the bleaching section was slightly more polluted than those from the pulping unit and this could be attributed to additional chemicals added after the pulping operation and the presence of microorganisms in the wastewater. Comparing with permissible standards set by the Federal Ministry of Environment (FMEnv) and National Environmental Standards and Regulations Enforcement Agency (NESREA) regulatory bodies, BOD_5, turbidity, COD, DO and pH from pulping were higher than the threshold values while others were within the stipulated regulatory limit. This could be linked to the use of virgin fibre from bamboo which contains less pollutant compared to other industries using waste papers from different sources.

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