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ORIGINAL RESEARCH ARTICLE

Assessment of the Physico-chemical Parameters and Heavy Metal Concentration of Delimi Wastewater in Jos North Local Government Area, Plateau State

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ABSTRACT

The high-water demand for domestic, agricultural, and industrial uses has increased water scarcity and is becoming alarming as natural or anthropogenic sources sometimes pollute the available water resources. Wastewater at Delimi was analyzed for physico-chemical parameters and heavy metal concentration before and after the discharge of effluents into the water. Standard analytical methods were employed to analyze the physico-chemical parameters, while the chemical analysis for the heavy metals was done using an Atomic Absorption Spectrophotometer (AAS). Results of the analysis showed the following ranges: temperature 20.30°C -24.40°C, pH 7.46 - 8.45, conductivity 310.40 - 481.68 µs/cm, total solids 318 - 481.00 mg/L, suspended solid 132.40 - 194.50 mg/L, dissolved solids 186. 40 - 287.00 mg/L, total hardness 496.20 - 651.00 mg/L, calcium hardness 121.37 - 147, 82 mg/L, magnesium hardness 103.00 - 124.00 mg/L, chloride 90.00 - 132.00 mg/L and sulphate 183.00 - 247.20 mg/L. All parameters assessed were within the WHO permissible limits except for chloride. Before the point of discharge, the wastewater recorded heavy metal concentration in the range of 0.00 – 5.80 ppm and 0.06 – 11.26 ppm after the point of effluent discharge. Iron recorded the highest value, which is above the WHO permissible limit, and lead, the lowest value, while Nickel and Manganese were not detected. Wastewater after the point of effluent discharge recorded higher concentration values, indicating the negative effects on the heavy metal concentration of the effluent discharges in the water. The resulting discharge increased the heavy metal concentration in the water, posing health challenges to the people within the environment. Using this wastewater for agricultural irrigation and laundry purposes could bring about exposure to heavy metals contained in it.

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KEYWORDS

Concentration; Delimi; Heavy metals; Physico-chemical; Wastewater; Pollution.

INTRODUCTION

Water is a limited resource frequently contaminated by human activities such as industrial, agricultural, and municipal waste. Nigeria is one of the nations in sub-Saharan Africa with records of poor water supply and accessibility to good sanitation (Shehu and Nazim, 2022). This has brought about a lack of clean water, hence the use of contaminated water for domestic, industrial, and agricultural purposes. Wastewater is a frequent means of transmission for illnesses including dysentery, cholera, and typhoid due to the presence of microorganisms (Tamunobereton *et al.*, 2013). Biological wastes deplete the oxygen in the sewage water through a natural mechanism that consumes it. Bacteria can take control of the sewage once water pollutants have used up all the oxygen. Water-soluble inorganic pollutants like caustic soda, salts (ammonium, nitrates, and phosphate salt), acids, and hazardous metals also form water pollutants (Vhahangwele and Khathutshelo, 2018). Some key nutrients also form pollutants that encourage algae growth and cause eutrophication (Akinnawo, 2023).

Heavy metals are environmental contaminants capable of causing human health problems if an excess amount is ingested through food (Sule *et al.*, 2021). Heavy metals are non-biodegradable and persistent metals with long biological half-life and can be bio-accumulated through the biological food chain (Riyam *et al.*, 2022; Sule *et al.*, 2021). Contaminated natural water bodies occur due to

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the introduction of unwanted or dangerous materials. (Henry, 2019; Jambeck *et al*., 2015). Heavy metals are metals with a high atomic weight and a density greater than 5 g/cm^3 (Zhang *et al*., 2019). Heavy metals are natural components of the earth's crust. They are released to the soil during naturally occurring phenomena like weathering and volcanic eruption (Ochelebe *et al.,* 2020) and released during mining activities within the earth's crust (Tehna *et al*., 2023).

Water pollution is the contamination of water bodies, usually due to human activities (Moss, 2008). Water pollution occurs when contaminants are introduced into the natural water body, introducing unwanted materials into natural water. Contaminated air, soil, and water by effluents from the industries are associated with heavy disease burden (WHO, 2002). Wastewater contains high levels of heavy metals that may pollute the environment once discharged into the water, air, or soil. These metals include As, Cr, Cu, Zn, Al, Cd, Pb, Fe, Ni, Hg, and Ag (Bahiru, 2020). In defining pollution, the water's intended use, degree of deviation from the norm, influence on public health, and ecological implications are all considered. High levels of heavy metals, certain radioactive isotopes, fecal coliform bacteria, phosphorous, nitrogen, and salts are among the contaminants in water. Heavy metals and pesticides are at the top of the list of toxicants in water bodies that pose serious environmental hazards to humans (Alengebawy *et al*., 2021). Bahiru (2020) expressed that industrial effluent discharged around the Eastern Oromia National region fields gave higher heavy metal concentrations. Henry (2019) reported in a published paper that wastewater discharge could have increased water temperature, conductivity, and higher heavy metal concentrations (Fe and Cl^-), which exceeded WHO permissible limits in the Yantika area of Plateau State.

Wastewater is water whose physical, chemical, or biological properties have been changed as a result of the introduction of certain substances, which renders it unsafe for some drinking, domestic, and other uses (Amoatey and Bani, 2011). It consists of liquid waste released from private homes, public buildings, businesses, and farms, and it can include a variety of possible pollutants and concentrations (Tilley *et al*., 2014). Wastewater may come from various places, including human waste, typically found in restrooms. This includes feces, used toilet paper, wipes, urine, and other biological fluids, also referred to as "black water". It can also refer to wash water (for clothes, floors, and dishes), "grey water," or sullage. Rainfall collected on roofs and hard-standings also form a part of this. Others are highway drainage, urban rainfall, and run-off from roads, car-parks, roofs, sidewalks, or pavements (contains oils, animal feces, liter, fuel residues, rubber residues, and metals from vehicle exhaust) (Gato-Trinidad, 2023).

This research aimed to determine the extent to which metal works have contaminated the wastewater in Delimi. Delimi is a location in Jos North Local Government Area of Plateau State where commercial activities of metal workshops, automobile vehicle repair, and other construction work occur. The waste product discharged from these activities and that of the domestic waste accumulates in the drainage. Bahiru (2020) reported that wastewater accumulates heavy metals that, when used for agricultural purposes, could lead to stunted plant growth and transmit heavy metals to man and animals. The wastewater quality before and after the point of discharge was evaluated for the presence of some heavy metals, such as copper, zinc, nickel, cadmium, lead, manganese, iron, and chromium, as well as other physico-chemical parameters, such as temperature, pH, conductivity, total hardness, dissolved and suspended solids, chlorides, calcium, and sulfate, in accordance with the standard analytical methods for the examination of water and wastewater. Analysis of Delimi wastewater effluent before and after the discharge spot will reveal the heavy metal concentration in the water, thereby discouraging farmers from using the water for irrigation purposes.

MATERIALS AND METHODS

Materials

The materials used for this research work include wastewater samples, polythene bottles, filter paper, distilled water, pH meter (Model 550), digital conductivity meter (Model 430), beakers, conical flasks, oven (Model: Mon-236), thermometer, desiccator, weighing balance (Model: BC ORMA Bilanc), EDTA, Calcium, Magnesium, UV-Visible spectrometer (Spec 222-2000 20D), Atomic Absorption Spectrophotometry (AAS, Perkin-Elmer). Conc. HNO_3.

Sample Collection

Wastewater samples were collected from Delimi wastewater in January 2022. Water samples were collected in polythene bottles previously washed with detergent, soaked in 50% concentrated nitric acid (HNO_3), and then rinsed several times with wastewater before sampling. The wastewater was collected before and after the spot of discharge of effluents, labeled properly, dated, and transported to the laboratory. The samples were stored at room temperature and analyzed for their pH, electrical conductivity, total dissolved solids, total suspended solids, calcium, magnesium, sulphate, and total solids, as well as the heavy metal concentration (Cu, Zn, Pb, Mn, Fe, Ni, Cr and Cd) using standard analytical methods.

Determination of Physical Parameters

Determination of Temperature and pH

The wastewater samples' temperature and pH were determined using a thermometer and digital pH meter (Model 550).

Electrical Conductivity (EC)

Specific conductivity was measured using a digital conductivity meter (Model 430).

Determination of Total Dissolved Solids (TDS)

TDS in the wastewater sample was quantified by gravimetric method. A clean Petri dish was heated to 100 °C in an oven, cooled in a desiccator, and then weighed to a consistent weight. The sampled wastewater sample was filtered into a clean conical flask using pre-weighed filter paper. The petri dish was filled with a known filtrate volume and heated in an oven at 180 °C. The obtained residue was cooled in the desiccator and weighed to a constant weight. The TDS was calculated with the formula below:

Total Dissolved solids (mg/L) = (A - B) × 1000/Volume of Sample (mL)

where A = weight of dried residue + evaporating dish (mg);

B = weight of the evaporating dish (mg) (Maliki *et al.*, 2020; Bhat *et al.*, 2018).

Determination of Total Suspended Solids (TSS)

TSS level in the collected water samples was determined using the gravimetric method. A pre-weighed glass fiber filter was used to filter a homogenous aliquot of water sample. Overnight, the filtrate was dried in an oven set at 105 °C. In a desiccator, the filter paper was removed, allowed to cool to room temperature, and weighed to a set weight. Later, the dried filter paper's increased mass was measured and used to calculate TSS. TSS was calculated using the formula:

Total suspended solids (mg/L) = (A - B) × 1000/Volume of Sample (mL)

Where A = weight of the filtrate after filtration (mg); B = weight of the filtrate before filtration (mg) (Ganoulis, 2009).

Determination of Total Solids (TS)

TS concentration in the water sample was determined by the gravimetric method. An aliquot of water sample was poured into a pre-weighed petri dish and heated in an oven at 180 °C. The residue was then cooled in the desiccator and weighed to a constant weight. TS is calculated with the formula:

Total solids (mg/l) = (A - B) × 1000/Volume of Sample (ml)

The addition of TSS and TDS could also determine TS.

Total Solids (mg/l) = Total Suspended Solids + Total Dissolved Solids (Kaur, 2010)

where A = weight of dried residue + evaporating dish (mg)

B = weight of the evaporating dish (mg) (WHO and UNICEF, 2017).

Total Hardness Determination

A complexometric titration of calcium and magnesium with an aqueous solution of the disodium salt of EDTA at a pH value of 10 was used to determine the overall hardness of water. The same theory underlies the detection of calcium when magnesium is present but at a pH level of 12. Magnesium ions precipitate in this situation as hydroxide and do not affect calcium measurement. The magnesium present in the sample may be calculated by subtracting the volume of EDTA solution required for the calcium determination from the volume required for the total hardness determination for equal sample volumes (Salvatore and Salvatore, 2015).

Determination of Calcium

Joseph et al. (2012) employed the method to determine the presence of calcium in the sample. About 50 mL of the sample was measured into a 250 mL conical flask and diluted to 100 mL with deionized water. Addition of 2 mL of 2 mol/L of NaOH solution was approximately done. The colour of the solution turned to claret or violet, and its pH value was measured to be 12.0. the content was titrated with EDTA solution to a distinct blue endpoint.

Determination of Magnesium

Joseph et al. (2012) described the method to determine magnesium in the wastewater sample. The magnesium present in the sample may be calculated by subtracting the volume of EDTA solution required for the calcium determination from the volume required for the total hardness determination for equal sample volumes.

Chloride Determination

Mohr's approach calculated the amount of chloride ions in the effluent. When titrating chloride ions with a silver nitrate standard solution, the Mohr technique employs chromate ions as an indicator. Titration was performed using a known volume of wastewater sample and a known quantity of silver nitrate. After all the chloride had been precipitated as white silver chloride, the first excess of titrant formed a brownish-red silver chromate precipitate, indicating the end point. The reactions are:

$$Ag + Cl^- \leftrightarrow AgCl \text{ (Ohioma et al., 2009).}$$

$$Ag_2CrO_{4_s} \leftrightarrow 2Ag^+ + CrO_4^{2-} \text{ (Sewvandi and Adikary, 2011)}$$

The chloride concentration in the wastewater was determined from the stoichiometry and moles consumed at the end point.

Sulphate Determination

The spectrophotometric approach was used to determine the sulphate content in the effluent at the Nigerian Institute of Geoscience, Tudun-Wada, Jos. Conditional reagents were made by combining the proper amounts of alcohol, concentrated HCl, distilled water, and chloride compound. A known volume of the wastewater sample and a blank were produced separately in flat bottom flasks, and 4.438 g of anhydrous sodium sulphate was dissolved in 500 mL of distilled water to provide a standard sulphate solution with a concentration of 100 mg/L. About 5 mL of the conditioning reagent was added to each flat bottom flask and topped up to 100 mL, after which 10 mg of barium chloride was added. When the solutions were turbid, a UV-Visible spectrometer (Spec 222-2000 20D) was used to detect the presence of sulphate at 420 nm. Using the graphical depiction of the standard solutions as a guide, the sulphate concentration in the wastewater sample was calculated (Tolulope *et al*., 2019).

Determination of Heavy Metal Concentration

The concentration of the heavy metals in the wastewater samples was analyzed at the Nigerian Institute of Mining and Geosciences, Tudun-Wada, Jos, using an Atomic Absorption Spectrophotometer (Model: 222-2000 20D) 55A using the method of AOAC (1995). The metals analyzed include Mn, Fe, Zn, Cu, Cr, Cd, Ni, and Pd. Clean and dry beakers were used, and exactly 100.00 ml of each sample was measured into the beaker and placed on a hot plate in a fume cupboard. The temperature of the hot plate was increased to around 230^0 C till no smoke was observed to be released, and the sample was then placed in a muffled furnace at a temperature of 250^0 C, later adjusted to 500^0 C and charred to ashes. The ash was gathered, and heat was applied at the range of 80-100^0C for 5 minutes after which it was cooled off, followed by adding 20 mL 1 Normal hydrochloric acid for digestion. The digested sample was filtered, and the filtrate was read off using a spectrophotometer. The absorbances were extrapolated using a standard curve for each heavy metal.

Statistical Analysis

Results obtained were expressed as mean (±) standard deviation from the mean with three replicates at $p \leq 0.05$ level of significance for each parameter measured. Statistical Package for Social Sciences (SPSS) Version 23 was used for the data analyses. Data generated for each parameter were subjected to a one-way Analysis of Variance (ANOVA) using Completely Randomized Design (CRD). Tukey test was used to separate means where a significant difference of $p < 0.05$ occurred.

RESULTS AND DISCUSSION

Result

Physico-Chemical Properties of Delimi Wastewater Before and After the Spot of Discharge

The result of the Physico-chemical parameters of the wastewater from Delimi before and after the spot of discharge is presented in Figure 1. The result showed significant differences among all the parameters observed in the experiment. The temperature, conductivity, total solids, suspended solids, and dissolved solids were significantly higher after the spot of discharge than the parameters before the spot of discharge. The pH, however, displayed a lower value (7.46±0.36 mg/L) before the discharge spot compared to the pH after the discharge spot (8.45±0.24 mg/L). The conductivity value before the discharge spot was lower (310.40±78.45 mg/L) than the result after the spot of discharge. Total solids (318.00±22.68 mg/L), suspended solids (132.40±8.11 mg/L), and dissolved solids (186.40±4.99 mg/L) were all significantly lower before the spot of discharge when compared to their values of 481.68±16.69 mg/L, 194.50±13.02 mg/L and 287±19.42 mg/L respectively after the discharge spot of discharge.

The chemical parameters of Delimi wastewater sample results before and after spots of discharge are displayed in Figure 1. The four parameters expressed significant differences between the two spots of discharge. The total hardness result (651±18.74 mg/L), calcium hardness (148.2±6.32 mg/L), and magnesium hardness (124±2.85 mg/L) showed a significantly higher result after the discharge spot compared to before the discharge spot discharge with values of 496.2±11.9 mg/L, 119±3.42 mg/L and 103±2.46 mg/L for total hardness, calcium hardness and magnesium hardness respectively. The chloride and sulphate concentrations in the wastewater showed that 90±5.43 mg/L and 183±4.18 mg/L were present before the spot of discharge, while 132±1.21 mg/L and 247.3±2.63 mg/L were present after the spot of discharge.

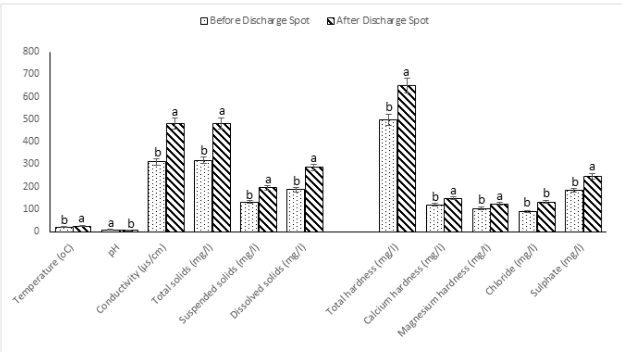

Figure 1: Physico-chemical Parameters of Delimi Wastewater before and after Discharge Spot

Heavy Metal Concentration

The result of the heavy metal concentrations before and after the spots of discharge showed that significant differences occurred among the present metals. The result, however, showed that manganese, nickel, and cadmium were not detected in the two samples before and after the discharge spots. The result of the iron, zinc, and copper showed higher concentrations (18.26±0.66, 0.23±0.02 and 0.19±0.01 respectively) after the discharge spot when compared with their concentrations before the discharge spot (5.80±0.26, 0.13±0.03 and 0.09±0.02 respectively).

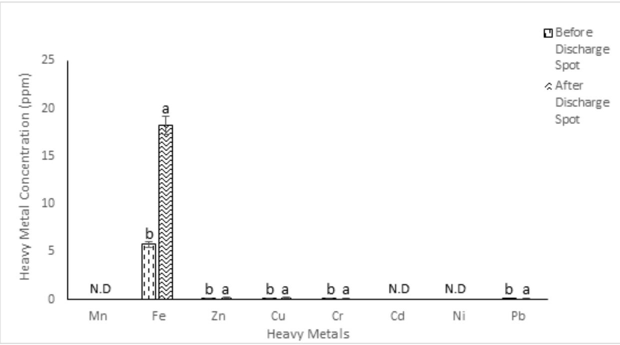

Figure 2: Heavy Metal Concentration in Delimi Wastewater Before and After Discharge Spot

Discussion

The chilly, dry winds common in the early hours may cause the low-temperature value measured for both the wastewater before and after the point of release. However, temperature levels of water samples were within the World Health Organization's recommended range of 10°C to 50 °C (WHO, 2006). The pH of effluents is very important as it can negatively impact the receiving watershed (Bhat *et al.*, 2018). Acidic pH is known to favour the bioavailability of most metals in rivers and its attendant consequences. Low pH can encourage the solubility of heavy metals resulting in the release of metal cations into the water rather than being absorbed in the sediment. Extreme low pH can bring about the migration of pH-tolerant algae, resulting in blooming algae (Raven *et al.*, 2020). The presence of alkaline compounds produced by the nearby metal workshop may cause the wastewater's somewhat alkaline pH value after the discharge.

It is well known that changes in dissolved solids' concentration significantly impact an aqueous solution's conductivity (Rebello *et al.*, 2020). A high degree of mineralization is indicated by high conductivity. However, the conductivities of both water samples were within the WHO-recommended limit of 810,000 μs/cm. The large-scale deposition of garbage and metal scraps into the water, which later corrode and disintegrate, may have contributed to the comparatively high concentration of total dissolved solids in the water beyond the point of discharge (Henry, 2019). This is clear from how far away the river is from the communities and the metal fabrication facilities. The total dissolved solids were within the 1000 mg/L WHO-recommended safe level. The liquid waste dumped from the locally manufactured metal drums later made its way into the wastewater, which might have caused the high concentration of total hardness discovered after the discharge point.

Water's capacity to dissolve calcium carbonates and magnesium carbonates is known to be enhanced by the presence of carbon dioxide in water. The comparatively high concentration of overall hardness in the water sample after the discharge point may also be attributable to the contribution of chemicals such as calcium and magnesium carbonates from effluents discharged into the water. Although WHO has not suggested an acceptable hardness level based on health guidelines, less than 75 mg/L of hardness may negatively affect the mineral balance. Given that very low or high concentrations of calcium (Ca) and magnesium (Mg) or total hardness in drinking water have been empirically recognized as the cause of the problems with corrosion, scaling, or taste of water (Kozisek, 2020), the increased calcium concentration in the water was likewise reflected in the concentration of overall hardness and could be due to the nature of the refuse dump generated in the vicinity of the study. Calcium is usually the primary cause of hardness in drinking water, and it ranges between 10-500 mg/L as $CaCO_3$ (Marier *et al.*, 1979).

Chloride is a crucial electrolyte in charge of controlling body fluids, delivering nerve impulses, and preserving acid-base balance in the body. It was reported that electrolyte imbalance results from excess chloride in the blood (Eshetu *et al.*, 2023). Elevated chloride levels in water bodies risk species' survival, development, and reproduction by endangering the sustainability of ecological food supplies (Tolulope *et al.*, 2019; Imo *et al.*, 2017). The permissible limit of chloride ions in drinking water is between 250-1000 mg/L (Kumar and Surajit, 2015). However, this value was high compared to the 159.50 mg/L reported in related research (Tolulope *et al.*, 2019). After the disposal point, the chloride content was relatively low (132 mg/L) compared to the permissible value above, making it tolerable. The chloride ions in the wastewater were also below the WHO-permitted limit of 250 mg/L.

Biogeochemical cycles rely heavily on sulphate in water in different environments. Sulphur is a crucial ingredient for the development of tissues in both plants and animals (Marcinkowska *et al.*, 2022). The wastewater's sulphate ion content varied from 183 mg/L before the point of effluent to 247 mg/L after the release point. The effluents discharged may be the cause of the high level of sulphate in the wastewater after the point of discharge. The sulfate value for this investigation was lower when compared to the value of 72.8 to 1434 mg/L published in related study (Tolulope, 2019). However, the sulphate ion content in the wastewater did not exceed the 250 mg/L permissible limits (WHO, 2006).

The concentration of manganese before and after the point of discharge of effluents was below detection. According to similar studies, water contains 42.77 ppm of manganese (Deshmukh, 2019; Henry, 2019). Tap water may taste, smell, and seem discolored when manganese concentrations exceed 0.05 mg/L (Hassan, 2008). Exactly 5.80 ppm and 11.26 ppm of iron were present before and after the discharge point. The runoffs from the local metal factory may be responsible for the elevated iron concentration. It could also be because of the metal containers dumped in the sewage or the iron remains from the metallic workshop since they corrode over time to release Fe ions. Iron levels in the wastewater exceeded the WHO-permitted limit of 0.1 ppm. The zinc (Zn) wastewater level before and after the discharge point was 0.13 ppm and 0.23 ppm, respectively. However, the amount of Zn in the wastewater was less than the 3.0 ppm WHO maximum acceptable level for drinking water. Before and after the discharge point, the wastewater copper content was 0.09 ppm and 0.19 ppm, respectively. The body needs Cu for optimum nourishment, but excessive amounts can harm the liver or induce anemia (Elarina *et al*., 2014). The corrosion of Cu pipes and scrap in the garbage dumps, which eventually erode into the water, may cause a high Cu concentration in the discharge point (Henry 2019). The WHO maximum limit of 2.0 ppm for Cu was not exceeded in any water sample. The wastewater Cr levels before and after the discharge site range from 0.12 ppm to 0.08 ppm. The Cr content before the point of discharge was higher than after the point of discharge of effluents. The activities of the metal workers and the kind of metal waste produced in the research area might have been responsible for the elevated Cr. According to Wijayawardena *et al*. (2016), trivalent Cr, which is minimally soluble in water, is necessary for human and animal lipid, glucose, and protein metabolism. However, the Cr content of the wastewater exceeded the 0.05 ppm WHO allowed limit. Cd was not detected before the effluent discharge but recorded a value of 0.06 ppm after the effluent discharge. This could be attributed to the activities of the metal workshop in the area. Even at very low concentrations, Cd can cause serious health issues if consumed (Henry, 2019; Wijayawardena *et al*., 2016). Cd affects cell proliferation, differentiation, and apoptosis. These activities interact with the DNA repair mechanism, generation of reaction oxygen species (ROS), and the induction of cell apoptosis (Rani *et al*. 2014). The wastewater before and after the discharge point did not contain any Ni. This may be because their concentrations are below the instrument's detection threshold. Pb concentration before and after the site of effluent release were 0.01 ppm and 0.07 ppm, respectively. Pb is the most significant hazardous heavy substance in the environment, and its use may be traced back to historical times because of its significant physico-chemical characteristics (Mahaffay, 1990). Pb damages the brain and central nervous system at high exposure levels, resulting in unconsciousness, convulsions, and even death. Children who recover from severe lead poisoning may, nevertheless, have behavioral and intellectual problems.

CONCLUSION

A body of water is deemed polluted and contaminated if the concentration of specific physico-chemical, biological, and metallic elements exceeds the World Health Organization's maximum permissible limit. The results of the physico-chemical parameters in Delimi wastewater demonstrated that the water before the point of discharge had a low pollution level because all of the parameters assessed were within the WHO permissible limit, except Fe and Cr, which exceeded the WHO permissible limit and the water after the point of discharge had a high pollution level because the concentrations of iron and chloride were higher than the WHO permissible limit. There is a need to discourage the use of this runoff water for agricultural and laundry purposes, as is the case, due to the detrimental effects of these heavy metals on plants and animals. Further studies are encouraged to create more awareness about the danger of wastewater in the Delimi area of Jos.

DECLARATIONS

Ethical Clearance

Not Applicable

Consent for Publication

All authors have read and consented to the publication of this manuscript.

Availability of Data and Materials

Not Applicable

Competing Interest

All authors declare that no competing interests occur among them.

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