

Application of *Moringa Oleifera* Seed Extract (*Mose*) in the Removal of Heavy Metals from Tannery Wastewater

M. A. Tanko¹, B. Y. Sanda^{2*}, M. H. Bichi³



^{1,3}Department of Civil Engineering, Bayero University Kano, Kano, Nigeria

²Department of Civil Engineering, Kebbi State University of Science and Technology Aliero, Kebbi, Nigeria.



ABSTRACT: The main focus of this research work is to investigate the possibility of applying *Moringa oleifera* seed extract for the removal of heavy metals from tannery wastewater. Samples were collected from effluent discharge points of the G_B tannery, Muhaza tannery and Z-tannery which are located in Challawa Industrial Area, Kano, Nigeria. The samples analyzed for physico-chemical parameters are pH, temperature, hardness, conductivity, turbidity, alkalinity, total suspended solid, total dissolved solid, calcium, magnesium, chloride, nitrates, sulphates and sulphide and heavy metals such as cadmium, chromium, copper, cobalt, iron, lead, manganese and zinc. The results show that the final levels of heavy metals after the application of *Moringa Oleifera* seed extracts were within NESREA acceptable limits. The heavy metal removal efficiencies were as follows; 99.29% for cadmium, chromium and iron while 96.03%, 95.56%, 96.84%, 87.41%, 91.35% for copper, cobalt, lead, manganese and zinc, respectively. The cheap, easy and environmentally friendly material called *Moringa oleifera* could be recommended to tannery companies for effective removal of heavy metals so as to have a safe, non-polluting environment and also prevent endangering the lives of aquatic organisms and humans.

KEYWORDS: *Moringa Oleifera*, tannery, wastewater, heavy metal, wastewater

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I. INTRODUCTION

Water is one of the essential materials required to sustain life and unfortunately has long been suspected of being the source of much of human illness. Surface and ground water have been increasingly contaminated due to increased industrial and agricultural activities. The public has been increasingly more demanding and engineers are expected to provide waters that are free of many physico-chemical and biological impurities. Increasing population with resultant increase in industrial operations, power production, vehicular traffic and new technologies have created new problems in water supply.

There is a need to understand contaminant fate and effects, as well as to acquire expertise in population control strategies beyond the conventional handling of effluent waste streams. The wide variety of heavy metals and organic chemicals produced and used by different industries has been shown to contaminate surface waters and ground water. These compounds are of public health concerns, and they also may have an adverse effect on the aquatic life.

The uncontrolled releases of waste effluents to large water bodies have negatively affected both water quality and aquatic life (Udosen 2006; Dan'azumi and Bichi, 2010 a, b). Tannery, is a place where animal skins are processed and transformed into leather.

Tannery wastewater contains heavy metals that do not decay and are toxic even at low concentrations. It is thus necessary to

remove them from the wastewater before disposal. Of the conventional treatments used for the removal of metals from liquid waste, chemical precipitation and ion exchange are the predominant methods. However, they have some limitations as they are uneconomical and do not completely remove metal ions, which make new removal processes necessary (Petroni 2000; Bai *et al.*, 2003, 2004).

As a result of this, local materials such as "*Moringa oleifera*" are being considered as a substitute. *Moringa oleifera* seeds extract has been a subject of research by several scholars in this regard (Bichi 2013). Jahn (1986) noted that *M. oleifera* is a single genus family of shrubs and trees cultivated in the whole of the tropical belt. In Northern Nigeria Sani (1990) reported the use of the leaves as vegetable and for medicinal purposes while the stem is used for demarcating landed properties. Many researchers have reported its use in surface water treatment (Muyibi *et al.*, 1995 a,b; Suarez *et al.*, 2005; Bichi, *et al.*, 2012).

This study therefore seeks to investigate the possibility of applying *Moringa oleifera* seed extract for the reduction or total removal of heavy metals in tannery wastewaters.

II. MATERIALS AND METHODS

This study was conducted in Challawa industrial area located in Kano, Northern Nigeria. It has a number of tanning and textile industries. Samples were collected from the effluent

*Corresponding author: sandabashir@gmail.com

of three major tanneries in the study area that discharge their wastewater into the adjoining water courses. The companies are GB-tannery Ltd., Muhaza Company Ltd., and Z-tannery Ltd.

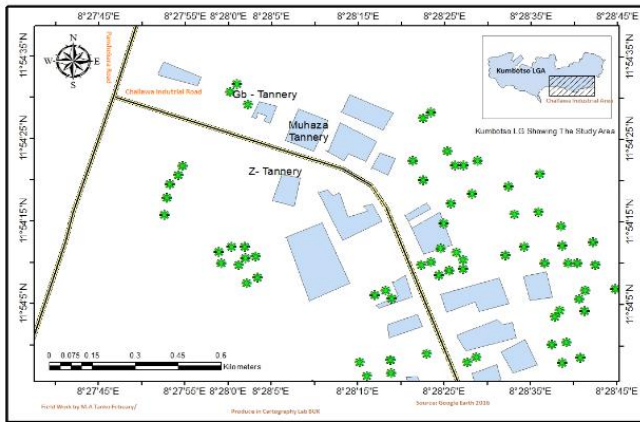


Figure 1: A Map Showing the Research Area.

A. Materials

Wastewater samples were collected at the main effluent from GB Tannery Limited, Muhaza Company Limited and Z-Tannery Limited. Sample collection was done by employing the standard procedure described by the Department of Waters Affairs and Forestry Pretoria (SA) DWAF (1992) in order to achieve an optimal level of success in sample collection. The following parameters were recorded at the site of collection: name of sample, time and date of collection, place of collection, pH, temperature, conductivity and turbidity. Ten liters (10L) plastic containers after being thoroughly washed with detergent rinsed with clean water and then distilled water then soaked in 5% HNO₃ for 24 hours were used to collect the wastewater samples. The samples were collected three times on weekly bases for each company and transported directly to Civil Engineering Laboratory, Bayero University Kano where it was stored in a refrigerator at a temperature below 4°C for further analysis. A large stock (5Kg) of good and high quality *Moringa oleifera* (Zogale seeds) was procured from Bayero University Kano (BUK) Farm.

B. Methods

1.) Method of *Moringa Oleifera* Seed Extract Preparation

Good quality of dry *Moringa oleifera* was selected and their Pod shells were removed manually and dried in an oven at 60°C for 24 hrs. Kernels was grounded in a domestic blender and sieved through 600 µm stainless steel sieve to obtain its powder.

An Aqueous extract was prepared using 200ml of distilled water and 25 g of *Moringa oleifera* seed powder, mixed by a magnetic stirrer for 60 minutes and allowed to settle for 20 minutes. *Moringa oleifera* aqueous extract was then finally filtered through 20 µm paper filter.

2.) Removal of Turbidity

This study consists of batch experiments involving rapid mixing, slow mixing and sedimentation. The apparatus consists of six beakers to be agitated simultaneously. 500 ml of the tannery wastewater samples was put in to each 6 one-liter beakers and placed under jar test apparatus.

Various doses of previously prepared *Moringa oleifera* seed extract; 125 mg/L, 250 mg/L, 375 mg/L, 500 mg/L, 625 mg/L and 750 mg/L) were added to the beakers containing 500ml of tannery wastewater. The jar tests were conducted with different rotating speed. This consisted of 100 rotations per minute, rpm for rapid mixing, for 1 minute and 30 rpm for 10 minutes for flocculation. After the agitation, the suspensions were allowed to settle for 20 minutes and about 100ml of the settled water was carefully decanted from the top of each beaker and its colour, turbidity, pH, alkalinity and heavy metals concentrations determined.

3.) Analyses of Heavy Metals

For the chemical analysis of the sample, the Open-Beaker Digestion (OBD) method was employed using HNO₃ as described in laboratory procedure for fertilizer and water analysis. The heavy metals were chromium, copper, cadmium, zinc, cobalt, iron, lead, and manganese in (mg/L) were carried out using an Atomic Absorption Spectrophotometer (AAS) and all concentrations were determined using the absorbance made with air-acetylene flame. The wastewaters were treated with different concentrations of the aqueous extract of *Moringa oleifera* and the results were then measured and analysed accordingly.

The analysis was carried out using an Atomic Absorption Spectrophotometer (Buck Scientific AAS, Model VGP 210) which is a selective and sensitive method used in the determination of metal and metalloids. All concentration was determined using the absorbance made with air-acetylene flame. Eight working solutions were prepared from stock solutions for each of the metals by successive serial dilution and each of the standard solutions was then aspirated into the flame of AAS.

Physico-chemical parameters determination such as pH, temperature, turbidity, settleable solids, suspended solids, dissolved solids, conductivity, hardness, alkalinity, chloride, sulphate, calcium were all carried out.

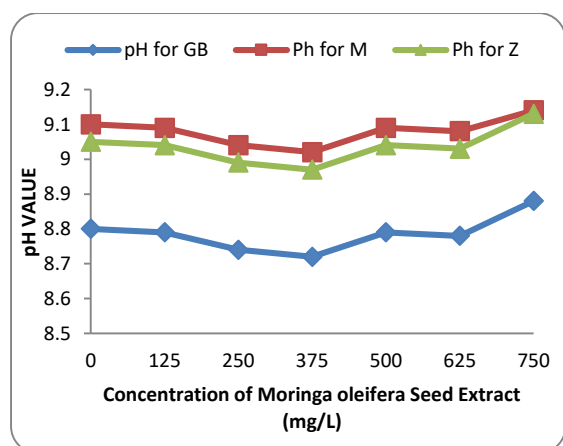
III. RESULTS AND DISCUSSION

The physicochemical and heavy metals parameters of the wastewater from the three (3) tanneries were determined. In comparison with the NESREA regulation for the maximum allowable concentration of heavy metals, it was found out that all the concentration exceeded the NESREA regulation except for temperature and pH. The presented in Table 1.

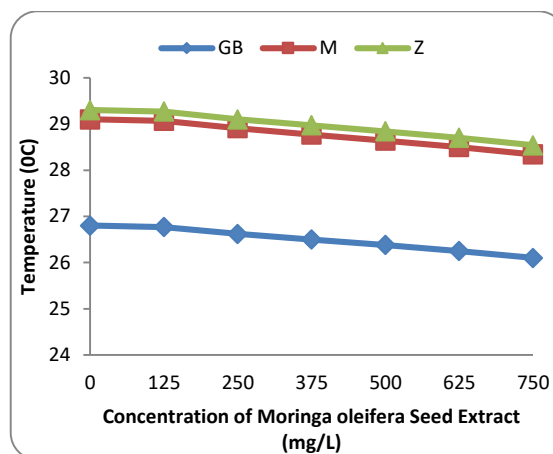
Table 1: Physicochemical and Heavy Metals Parameters in Tannery Wastewaters from G_B, Muhaza (M) and Z-Tanneries Limited (Z).

S/No	Parameters	NESREA Regulations on Tannery Effluent	G _B	M	Z
1	pH	6-9	8.80	9.10	9.05
2	Temperature (°C)	40	26.80	29.1	29.30
3	Hardness (mg/l)	-	228.2	187.6	159.8
4	Conductivity (µS/cm)	-	2,650	2,780	2480
5	Turbidity (NTU)	-	871	928	793
6	Alkalinity (mg CaCO ₃ /l)	-	709	1,025	845
7	Total Suspended Solids (mg/l)	25	489	567	523
8	Dissolved Solids (mg/l)	2000	2,667	2,586	2,534
9	Calcium (mg/l)	-	102.8	98.42	105.1
10	Magnesium (mg/l)	-	6.80	8.40	10.90
11	Chloride (mg/l)	0.5	206.9	109.1	147.2
12	Nitrates (mg/l)	-	34	29	28
13	Sulphates (mg/l)	-	734	876	930
14	Sulphide (mg/l)	1	130	198	150
15	Cadmium (mg/l)	0.02	16.40	11.80	12.89
16	Chromium (mg/l)	0.1	9.80	8.70	8.98
17	Copper (mg/l)	0.5	5.80	4.40	3.97
18	Cobalt (mg/l)	0.5	1.80	1.90	2.85
19	Iron (mg/l)	-	1.40	1.10	1.49
20	Lead (mg/l)	0.1	1.90	1.40	1.73
21	Manganese (mg/l)	1.0	2.70	3.00	1.99
22	Zinc (mg/l)	2	10.40	11.20	9.93

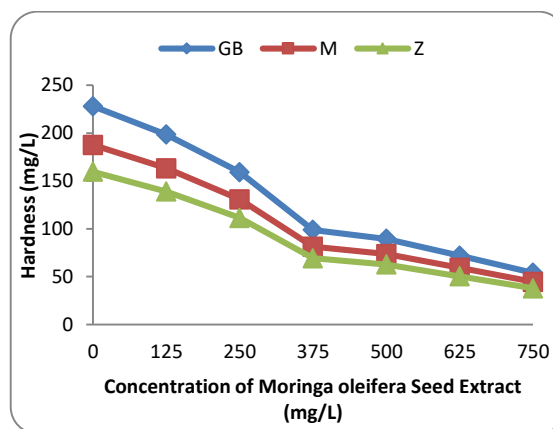
pH value for G_B tannery was found within the guideline range of 6-9, Muhaza tannery exhibits a pH of alkaline range while Z-tannery exhibits the same trend. It was observed that *Moringa oleifera* seed extract had no much effect on this parameter unlike other physicochemical parameters as in Figure 2.

**Figure 2: pH Chart for G_B, Muhaza and Z-Tanneries Limited.**

The temperature of the G_B tannery was in the range of 26.10 °C – 26.77 °C with the control sample of 26.80 °C, Muhaza tannery's temperature was in the range of 28.34 °C – 29.07 °C with the control sample of 29.10 °C and Z-tannery temperature was in the range of 28.54 °C – 29.27 °C with the control sample of 29.30 °C. All temperatures were lower than 40 °C guideline for wastewaters as clearly shown in Figure 3.

**Figure 3: Temperature Chart for G_B, Muhaza and Z-Tanneries Limited.**

The hardness of water samples with initial concentrations of 228.20mg/L, 187.60mg/L and 159.80mg/L from the three tanneries in question were found reduced with the effect of *Moringa oleifera* seed extract although no guideline value was specified for hardness by the agency and this could be as a result of coagulation mechanism of *Moringa oleifera* coagulant protein which described it as an adsorption, charge neutralization and inter particle bridging as shown in Figure 4.

**Figure 4: Hardness Chart for G_B, Muhaza and Z-Tanneries Limited.**

The conductivity exhibited by Muhaza tannery was found to be the highest with a value of 2780 µS/cm followed by G_B tannery with a value of 2650µS/cm and Z-tannery with a value of 2480 µS/cm but with the aid of *Moringa oleifera* seed extract the values were found below 2000 µS/cm even though no guideline figure was specified for the conductivity by the

agency. These can be related to the high concentration of total dissolved solids in the three tanneries as shown in Figure 5.

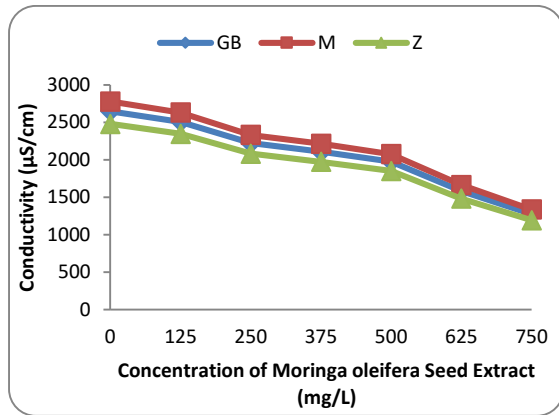


Figure 5: Conductivity Chart for GB, Muhaza and Z-Tanneries Limited.

The turbidity of Muhaza tannery with the value of 928 NTU was found to be the highest followed by that of GB tannery 871 NTU and Z-tannery 793 NTU and this can be attributed to the high concentration of suspended solids in the samples. No guideline value was given for the turbidity by the agency but at the end of the experimental test, the value of turbidity reduced consistently for the three tanneries at optimum dosage of 500 mg/L before it later rose when 625 mg/L extract was added which shows there is destabilization of the flocks due to excess positive ions in the *Moringa oleifera* seed extract and its very efficient in turbidity removal, Although, it was observed that a more settling time is required after 500 mg/L addition of the extract as shown in Figure 6.

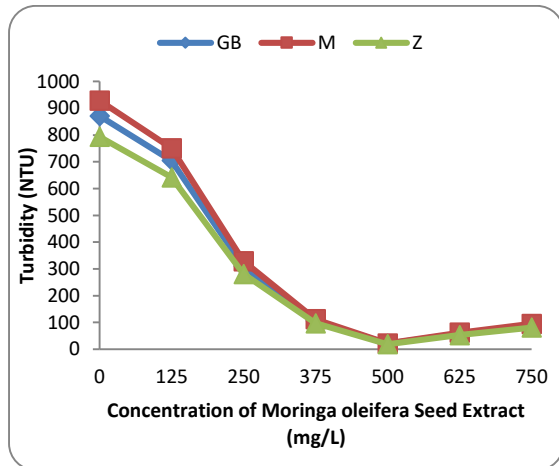


Figure 6: Turbidity Chart for GB, Muhaza and Z-Tanneries Limited.

The Alkalinity in mg/L of CaCO₃ in the tannery wastewaters were higher in Muhaza tannery with a control sample of 1025 mg/L, 845 mg/L for Z-tannery and 709 mg/L for GB tannery but at the end of the laboratory test, the values were dropped with the effect of *Moringa oleifera* seed extract as shown in Figure 7.

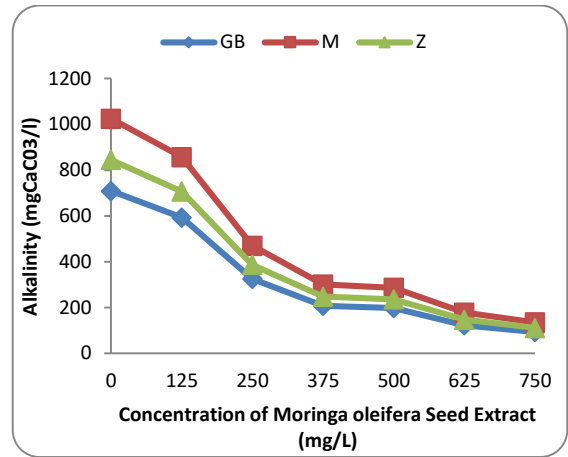


Figure 7: Alkalinity Chart for GB, Muhaza and Z-Tanneries Limited.

The suspended solids in tanneries in question were significantly higher than the 25 mg/L National Environmental Standards and Regulations Agency (NESREA) guideline for tannery water, while Muhaza tannery exhibits higher control sample of 567 mg/L but was reduced at the end of the test to 22.03 mg/L at 625 mg/L. It was observed that the soluble particles in the water attach to the active agent of *Moringa oleifera* seed extract that bond them together creating large flocs in the water as shown in Figure 8.

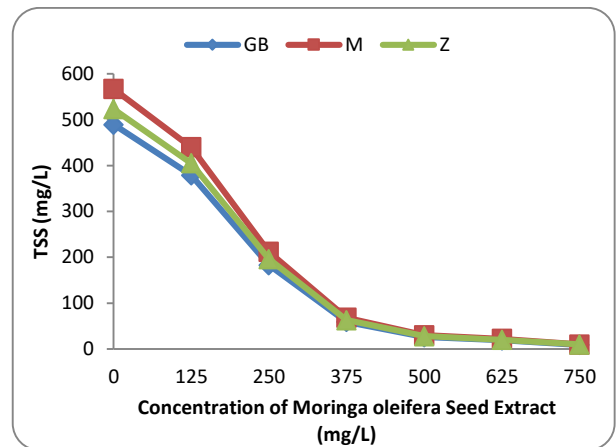


Figure 8: Total Suspended Solid Chart for GB, Muhaza and Z-Tanneries Limited.

The concentration of total dissolved solids was not in conformity with NESREA guideline as all values were greater than 2000 mg/L. The highest concentration was observed in GB tannery with a concentration of 2667 mg/L followed by Muhaza tannery having a TDS concentration of 2586 mg/L, the least TDS concentration was observed in Z-tannery with a value of 2534 mg/L, while their TDS concentrations were found reduced below the stated guideline at the end of the experiment as shown in Figure 9.

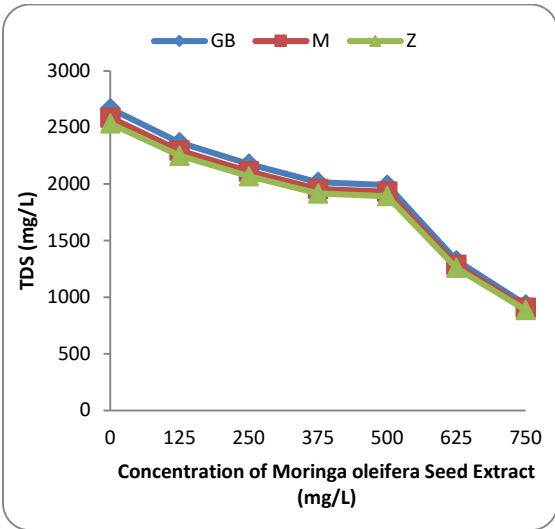


Figure 9: Total Dissolved Solid Chart for G_B, Muhaza and Z-Tanneries Limited.

The concentration of calcium in Z-tannery exhibits highest value of 105.1 mg/L, 102.8 mg/L for G_B tannery and 98.42mg/L for Muhaza tannery wastewaters, while all were reduced far below the values of their control samples at various percentages of *Moringa oleifera* seed extract as shown in Figure 10.

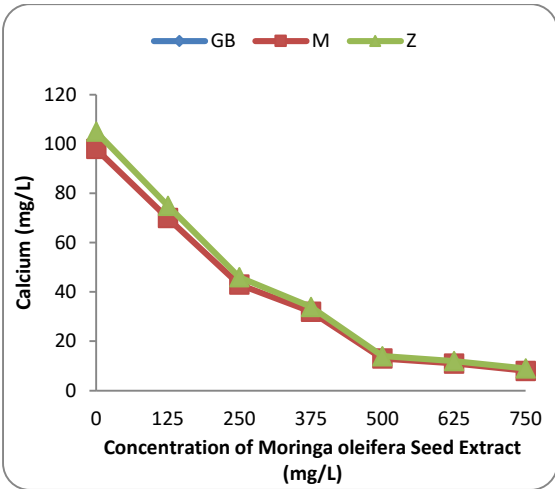


Figure 10: Calcium Chart for G_B, Muhaza and Z-Tanneries Limited.

The magnesium content of G_B tannery, Muhaza tannery and Z-tannery were found to be 6.8 mg/L, 8.4 mg/L and 10.9 mg/L respectively. The concentrations were reduced at the end of the experiment with the variation in the dosages of *Moringa oleifera* as shown in Figure 11.

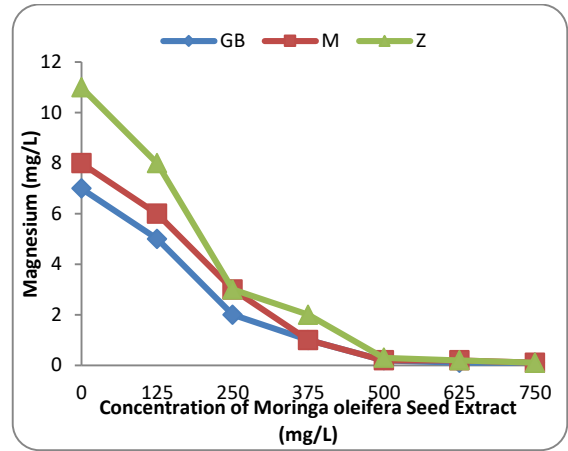


Figure 11: Magnesium Chart for G_B, Muhaza and Z-Tanneries Limited.

The chloride concentration obtained in most of the tannery wastewater samples were higher than the NESREA guideline value of 0.5 mg/L, with the G_B tannery exhibits much higher concentrations of 206.9 mg/L followed by Z-tannery exhibits 147.2mg/L and then Muhaza tannery exhibits 109.10 mg/L. The concentrations were reduced below the guideline value at 750 mg/L of *Moringa oleifera* seed extract as shown in Figure 12.

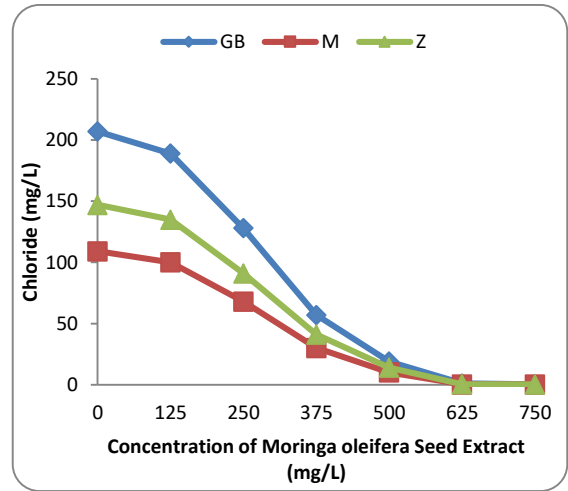


Figure 12: Chloride Chart for G_B, Muhaza and Z-Tanneries Limited.

The nitrates concentrations of G_B tannery, Muhaza tannery and Z-tannery were found to be 34.00 mg/L, 29.00mg/L and 28.00 mg/L respectively. The concentrations were reduced at the end of the experiment with the variation in the dosages of *Moringa oleifera* seed extract as shown in Figure 13.

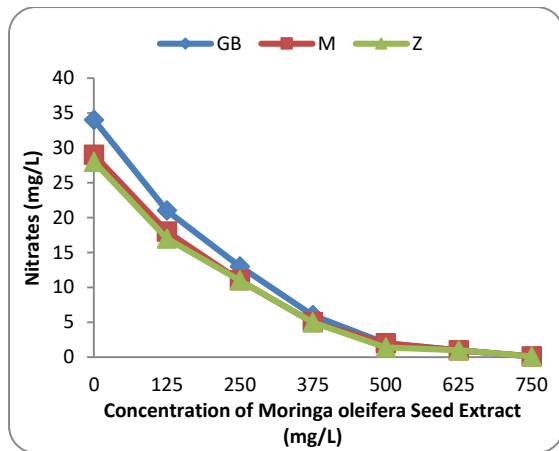


Figure 13: Nitrates Chart for G_B, Muhaza and Z-Tanneries Limited.

The sulphates concentration seems to be much from Z-tannery sample with a control sample of 930 mg/L followed by Muhaza tannery with a control sample of 876 mg/L and G_B tannery with a control sample of 734mg/L. The concentrations reduced to minimal level compare to their initially exhibited values as shown in Figure 14.

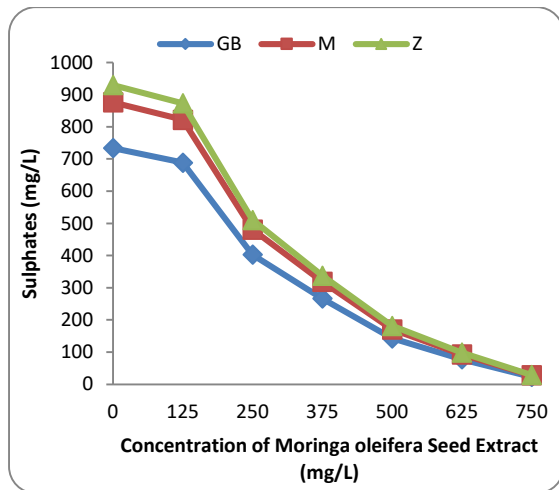


Figure 14: Sulphates Chart for G_B, Muhaza and Z-Tanneries Limited.

The concentration of sulphides was higher for the three tanneries than 1mg/L NESREA value with Muhaza tannery exhibits higher concentration value of 198 mg/L, followed by Z-tannery exhibits 150 mg/L and G_B tannery exhibits 130 mg/L. The concentrations were reduced below the guideline value at 750 mg/L of the *Moringa oleifera* seed extract as shown in Figure 15.

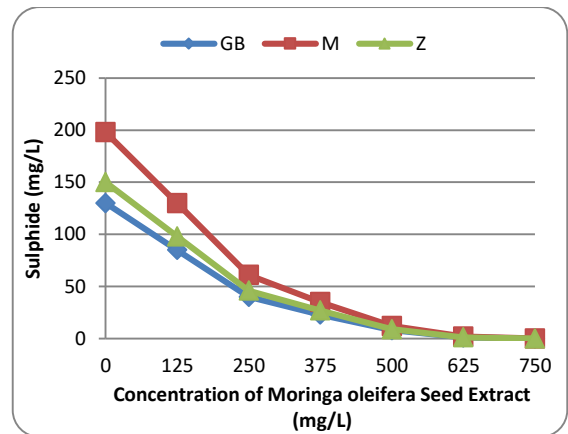


Figure 15: Sulphide Chart for G_B, Muhaza and Z-Tanneries Limited.

The concentration of cadmium in G_B, Muhaza and Z-tanneries were found to be 16.40 mg/L, 11.80 mg/L and 12.8 mg/L respectively which was significantly higher than the NESREA guidelines for tannery wastewater of 0.02 mg/L. The concentration of cadmium was reduced from 16.40mg/L – 0.01 mg/L, 11.80 mg/L – 0.01 mg/L and 12.89 mg/L – 0.01 mg/L for G_B, Muhaza and Z-tanneries respectively at 750 mg/L of *Moringa oleifera* seed extract and its obviously shows an efficient removal of cadmium for the three tanneries as follows; 99.94%, 99.94% and 99.92% respectively. It was observed that *Moringa oleifera* consists of adsorption and neutralization of the colloidal positive charges that attract the negatively charged impurities and metals in water as shown in Figure 16.

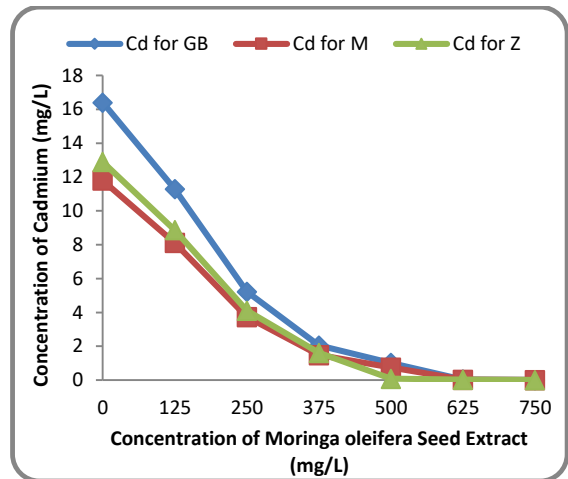


Figure 16: Cadmium (Cd) Chart for G_B, Muhaza and Z-Tanneries Limited.

The concentration of chromium in G_B, Muhaza and Z-tanneries were found to be 9.80 mg/L, 8.70 mg/L and 8.98 mg/L respectively which was significantly higher than the NESREA guidelines for tannery wastewater of 0.1 mg/L. The concentration of chromium was reduced from 9.80 mg/L – 0.07 mg/L, 8.70 mg/L – 0.06 mg/L and 8.98 mg/L – 0.06 mg/L for the three tanneries at 625 mg/L of *Moringa oleifera* seed

extract and therefore shows an efficient removal of chromium at 99.29%, 99.31% and 99.93% respectively. It was observed that *Moringa oleifera* consists of adsorption and neutralization of the colloidal positive charges that attract the negatively charged impurities and metals in water as shown in Figure 17.

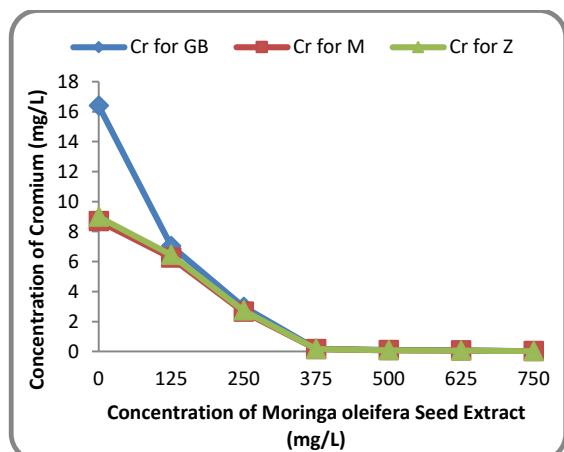


Figure 17: Chromium (Cr) Chart for G_B, Muhaza and Z-Tanneries Limited.

The concentration of copper in G_B, Muhaza and Z-tanneries were found to be 5.80 mg/L, 4.40 mg/L and 3.97 mg/L respectively which was significantly higher than the NESREA guidelines for tannery wastewater of 0.5mg/L. The concentration of copper was reduced from 5.80mg/L – 0.23mg/L, 4.40 mg/L – 0.18 mg/L and 3.97 mg/L – 0.16 mg/L for the three tanneries at 500 mg/L of *Moringa oleifera* seed extract and this clearly shows an efficient removal of copper at 96.03%, 95.91% and 96.00% respectively. It was observed that *Moringa oleifera* consists of adsorption and neutralization of the colloidal positive charges that attract the negatively charged impurities and metals in water as shown in Figure 18.

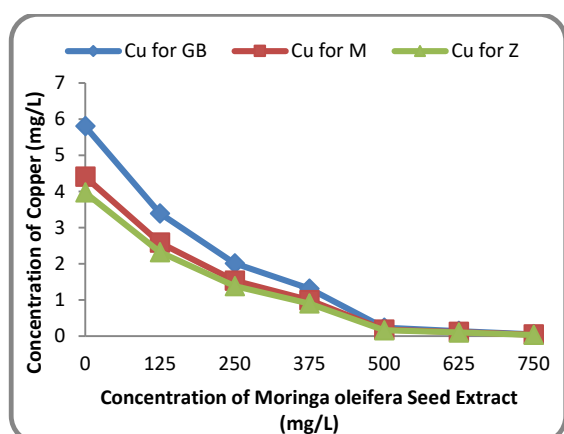


Figure 18: Copper (Cu) Chart for G_B, Muhaza and Z-Tanneries Limited.

The concentration of cobalt found in G_B tannery, Muhaza tannery and Z-tannery was significantly higher than the NESREA guidelines for tannery wastewater of 0.5 mg/L, with the G_B tannery exhibiting a higher value of 1.80 mg/L, Muhaza

tannery exhibiting a value of 1.90mg/L and Z-tannery was found to be 2.85 mg/L respectively. The concentration of cobalt reduced from 1.80 mg/L – 0.08 mg/L, 1.90 mg/L – 0.08 mg/L and 2.85 mg/L – 0.13 mg/L at 375 mg/L of *Moringa oleifera* seed extract and this shows an efficient removal of cobalt at 95.56%, 95.79% and 95.55% respectively from tannery waste water. It was observed that *Moringa oleifera* consists of adsorption and neutralization of the colloidal positive charges that attract the negatively charged impurities and metals in water as shown in Figure 19.

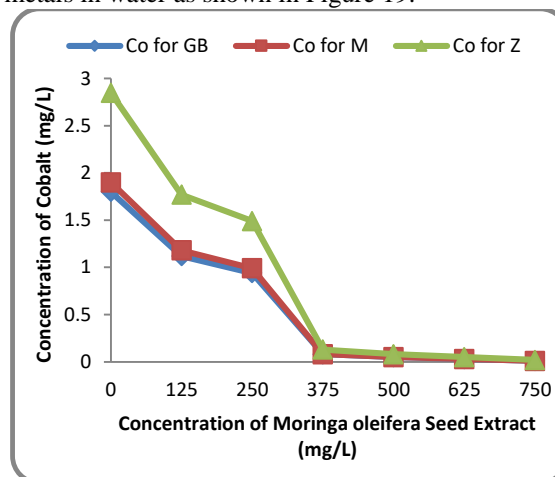


Figure 19: Cobalt (Co) Chart for G_B, Muhaza and Z-Tanneries Limited.

Although, the concentration of iron was not specified by NESREA agency for tannery wastewater but metal iron exhibiting a higher value of 1.4 mg/L in G_B tannery, Muhaza tannery exhibiting a value of 1.10 mg/L and Z-tannery exhibiting 1.49 mg/L and at the end of the research the concentration of iron reduced from 1.40 mg/L – 0.01 mg/L, 1.10 mg/L – 0.01 mg/L and 1.49 mg/L – 0.01 mg/L at 500 mg/L of *Moringa oleifera* seed extract and this shows an efficient removal of iron at 99.29%, 99.09% and 99.33% respectively from tannery waste water. It was observed that *Moringa oleifera* consists of adsorption and neutralization of the colloidal positive charges that attract the negatively charged impurities and metals in water as shown in Figure 20.

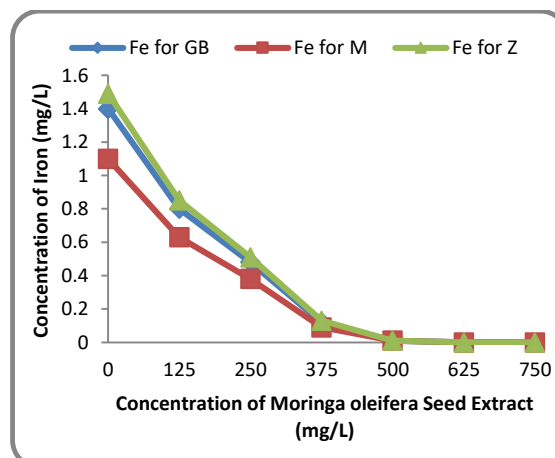


Figure 20: Iron (Fe) Chart for G_B, Muhaza and Z-Tanneries Limited.

The concentration of lead found in G_B tannery, Muhaza tannery and Z-tannery was significantly higher than the NESREA guidelines for tannery wastewater of 0.1 mg/L, with the G_B tannery exhibiting a higher value of 1.90mg/L, Muhaza tannery exhibiting a value of 1.40 mg/L and Z-tannery was found to be 1.73 mg/L respectively. The concentration of lead reduced from 1.90 mg/L – 0.06mg/L, 1.40 mg/L – 0.04 mg/L and 1.73 mg/L – 0.06mg/L at 500mg/L of *Moringa oleifera* seed extract and this shows an efficient removal of lead at 96.84%, 97.14% and 96.53% respectively from tannery waste water. It was observed that *Moringa oleifera* consists of adsorption and neutralization of the colloidal positive charges that attract the negatively charged impurities and metals in water as shown in Figure 21.

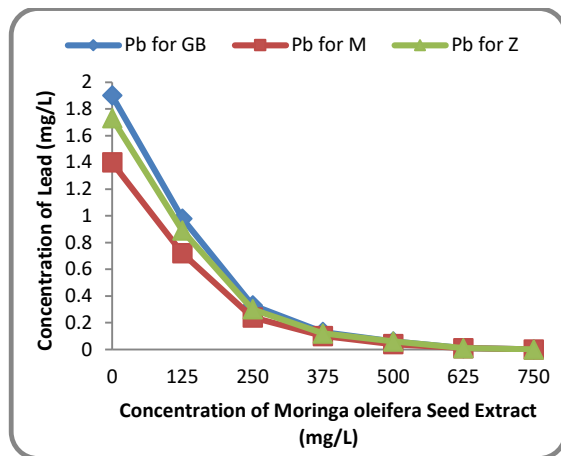


Figure 21: Lead (Pb) Chart for GB, Muhaza and Z-Tanneries Limited.

The concentration of manganese found in G_B tannery, Muhaza tannery and Z-tannery was significantly higher than the NESREA guidelines for tannery wastewater of 1.0mg/L, with the G_B tannery exhibiting a higher value of 2.70 mg/L, Muhaza tannery exhibiting a value of 3.00mg/L and Z-tannery was found to be 1.99mg/L respectively. The concentration of manganese reduced from 2.70 mg/L – 0.34 mg/L, 3.00 mg/L – 0.38 mg/L and 1.99 mg/L – 0.25 mg/L at 375 mg/L of *Moringa oleifera* seed extract and this shows an efficient removal of cobalt at 87.41%, 87.33% and 87.44% respectively from tannery waste water. It was observed that *Moringa oleifera* consists of adsorption and neutralization of the colloidal positive charges that attract the negatively charged impurities and metals in water as shown in Figure 22.

The concentration of zinc found in G_B tannery, Muhaza tannery and Z-tannery was significantly higher than the NESREA guidelines for tannery wastewater of 2.00 mg/L, with the G_B tannery exhibiting a higher value of 10.40 mg/L, Muhaza tannery exhibiting a value of 11.20 mg/L and Z-tannery was found to be 9.93 mg/L respectively. The

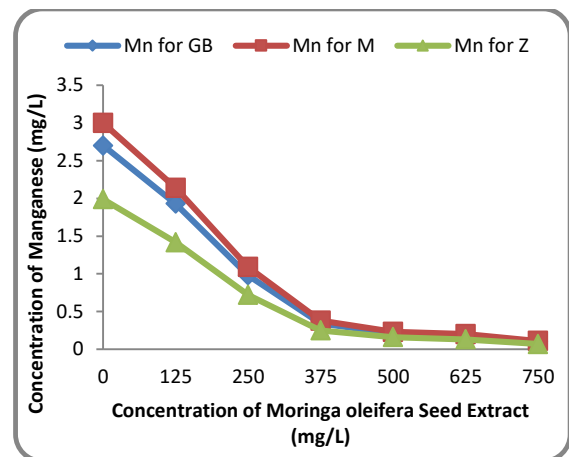


Figure 22: Manganese (Mn) Chart for G_B, Muhaza and Z-Tanneries Limited.

concentration of zinc reduced from 10.40 mg/L – 0.90 mg/L, 11.20 mg/L – 0.97 mg/L and 9.93 mg/L – 0.86 mg/L at 500 mg/L of *Moringa oleifera* seed extract and this shows an efficient removal of zinc at 91.35%, 91.34% and 91.34% respectively from tannery waste water as shown in Figure 23.

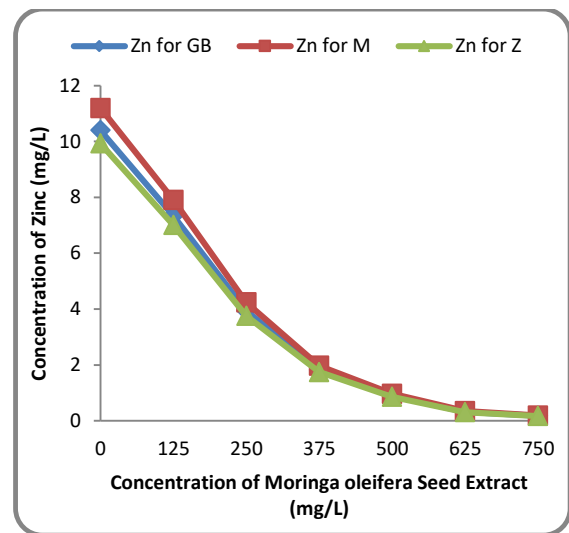


Figure 23: Zinc (Zn) Chart for G_B, Muhaza and Z-Tanneries Limited.

IV. CONCLUSION

Based on the study test results, the following conclusions were drawn.

- The study showed efficient removal of heavy metals from the three tannery wastewater using seed extract and gave the removal efficiency as follow; cadmium, chromium, and iron were reduced below the guidelines at the same removal efficiency of 99.29% while copper, cobalt, lead, manganese and zinc reduced at 96.03%, 95.56%, 96.84%, 87.41% and 91.35% respectively. Therefore, it can be concluded that *Moringa oleifera* seed extract can

effectively be used to remove heavy metals from tannery wastewater.

- b) The optimum dosages of various *Moringa oleifera* seed extract were found to be 750 mg/L for cadmium, 625 mg/L for chromium, 500 mg/L for copper, iron, lead and zinc while 375 mg/L for manganese and cobalt for wastewater samples containing heavy metal concentrations in G_B tannery, Muhaza tannery and Z-tannery industries. This study revealed a significant reduction of both physicochemical and heavy metal parameters of tannery wastewater when treated with the *Moringa oleifera* seed extract.

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