

Physicochemical Characterization and Assessment of Ecological Risk of Heavy Metals in Tin Mine Tailings in Riyom Local Government Area of Plateau State, Nigeria

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Abstract

In this study, a non-destructive analytical techniques (Energy dispersive X-Ray fluorescence) was used to analyze the concentration of seven heavy metals (Pb, Cr, As, Ni, Cd, Cu and Zn) in tin mine tailing from mining and control sites in Rim, Sharubutu and environs. The physicochemical results showed the pH for S1 and S2 from the mining and control sites were (5.31 and 4.97) and (6.32 and 5.71) respectively indicating that the mine sites is more acidic than the control sites. While their bulk density and electrical conductivity was good for planting. The concentration of the heavy metals were within the maximum permissible limits except for Pb and As in mining and control sites of range (270-300) mg/kg and (60-80) mg/kg, which are above the permissible limits (80 mg/kg and 0.07 mg/kg) respectively. This could be attributed to the mining activities and atmospheric depositions on the sites. The enrichment factor values for Pb, Cr, As, Ni, were S1 (1.07, 1.18 1.14 and 1.14) respectively while Cd, Cu and Zn were not detected, S2 (1.11, 1.19, 1.33, 1.14 and 1.11) for Pb, Cr, As, Ni, and Zn respectively, while Cd and Cu were not detected. The geo accumulation factor for S1 were (0.22, 0.24, 0.23 and 0.23) for Pb, Cr, As and Ni, while Cd, Cu and Zn were not detected, S2 (0.22, 0.24, 0.27, 0.23 and 0.22) for Pb, Cr, As, Ni, and Zn respectively, while Cd and Cu were not detected. This indicates environmental pollution. The result obtained for risk index Ri where S1 (24.81) and S2 (28.04), these shows that the risk index of heavy metals in tin mine tailings of the studied areas posed low ecological risk to the ecosystem. The Fourier transform infra-red (FTIR) spectra analysis shows the functionality of Ag⁺, Ca²⁺, K⁺, and Mg²⁺ were within the band range of 700-2200 cm⁻¹. S1 showed absorption bands at (779.0 cm⁻¹) for silver bromate, (1038.2 cm⁻¹) for calcium sulphate and potassium metaborate, (2108.7 cm⁻¹) for magnesium per chlorate and sodium chromate. S2 showed absorption band at (2173.0 cm⁻¹) for magnesium per chlorate and sodium chromate. The surface morphology of the tin mine tailings through the use of Scanning electron microscopy (SEM) technique revealed Homogeneous small size and heterogeneous crystalline irregular shape.

Keywords: Tin mine tailings; Heavy metals; Geo accumulation index; Enrichment factor and risk index

Introduction

Human activities, such as mining, smelting, fossil fuel combustion, agricultural practices and waste disposal and extraction of metal ore, has resulted into high multi-elemental contamination of the environment by heavy metals from parent materials [1,2]. These activities have drastically altered their geochemical cycles and biochemical balance and caused dis-equilibrium of the terrestrial ecosystem due to excavation of large amount of sand and the eventual accumulation of large volume of tailings [3].

Tailings, also called mine dumps, culm dumps, slimes, tails, refuse, leach residue or slickens, are the materials left over after the process of separating the valuable fraction from the unvaluable/uneconomic fraction (**gangue**) of an ore [4]. These tailings usually contain high concentrations of toxic or poisonous heavy metals and irreclaimable reagents and chemicals used in the extraction processes, which tend to increase the natural metal content of the soil with such

as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb).

In the twentieth century, Nigeria was one of the world's major tin producing countries though production later decline towards the end of the century but tin mining activities are still on. Besides tin, tin mining produces tin tailings, a by-product of rough concentrates of cassiterite. The amount of tailings can be large, ranging from 90-98% for some copper ores to 20-50% of the other (less valuable) minerals [5]. These tailings from tin mining industry were usually processed to extract valuable minerals such as columbite, ilmenite, monazite, zircon, xenotime and struverite. The mentioned minerals had been observed to contain high concentrations of ⁴⁰K, ²²⁶Ra and ²³²Th, which are naturally occurring radionuclides in the environment plus other host of toxic heavy metals [6,7]. Serious environmental impact like the destruction of natural soil, extraction of important volumes of materials and elevated levels of trace elements are common characteristics of most mine tailings [8].

Heavy or toxic metals could also be trace elements that are non-biodegradable and indiscriminate dumping of tailings from mining sites will lead to **bioavailability** and bioaccumulation in the soil, surface

water and natural vegetation. The most critical effects of this pollution occur when toxic waste accumulates in farmlands. High concentration of these metals in soil may cause long-term risk to ecosystems and humans [8].

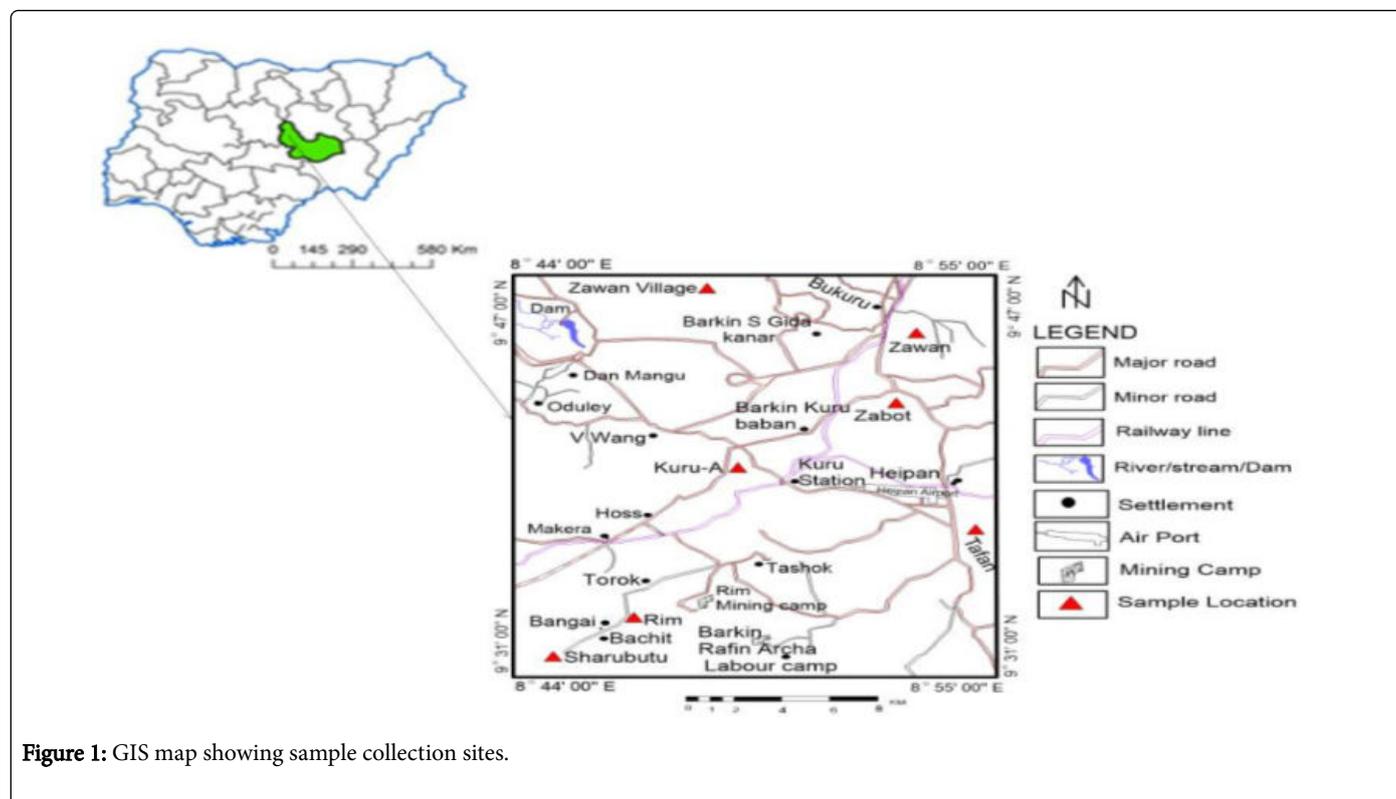
Research Methodology

Sample location and site description

This research work was carried out in Rim and Sharubutu of Riyom Local Government Area of Plateau State, Nigeria. Plateau state is located in the middle belt of Nigeria's with an area of 30.91 km (11936 sq mi), the state has an estimated population of about three million people. It is located between latitude 9°51'30"N to 10°2'00"N and

longitude 8°48'00"E to 9°51'00"E. The name Plateau state emerged due to its mountainous topography with captivating rock formations. The mountains attitude ranges from around 1,200 meter (about 400 feet) to a peak of 1,829 meters above sea. The predominant occupation of the people here is mining and subsistence farming, 50 g of the sample was taken.

Figure 1 showed the sampling points where the tailing samples were taken from in Riyom L.G.A. of Plateau State. The Geographical Positioning System (GPS) was used to locate the sampling area to ensure consistency. Each sample was taken from the mining site in Sharubutu (S1) and Rim (S2) of Riyom Local Government Area of Plateau State, Nigeria.



Sample preparation

Two samples of 50 g each were taken from the mining and the control site respectively. The Tin mine tailing and soil samples was pretreated through washing, drying and in some cases grinding to size particles of 2 mm to distinguish between small and large particles. The goal of a pretreatment procedure was to prepare a test sample in which the concentration in the original soil provided however, this procedure did not alter chemical specie analyzed.

Determination of physiochemical parameters of tin mine tailings and soil samples

The physiochemical parameters such as pH, conductivity and bulk density of tin mine tailing and soil samples were carried out using standard laboratory procedures.

Tailings bulk density

The tailing bulk density (BD) also known as bulk dry density, is the weight of dry tailings divided by the total tailings volume. The total tailings volume is the combined volume of solids and pores which may contain air or water or both [9].

Tailings pH and electronic conductivity

The determination of tailing pH required that the slurry be prepared using the homogenized tailings sample and deionized water. The sample slurry was prepared by adding 20 mL of deionized water to the 20 g scope of the sample in the beaker. Each sample was vigorously stirred for 15 minutes with a glass stirring rod and let to stand for 30 minutes. The pH meter was calibrated over the appropriate between the acidity and alkaline range of 2.00 to 12.00 using the buffer standard solution. The pH and electrical conductivity (EC) rods were then immersed into the beaker with slurred samples.

The pH of the tailings and its corresponding EC were then recorded from the pH meter and from the electrical conductivity meter (model HI86304) respectively.

Elemental analysis

The heavy metal concentration in tailings was determined in the laboratory using Energy dispersive X-ray fluorescence spectrometer EDX-XRF (MiniPAL4). The tailings samples were prepared to allow direct XRF analysis on solid powdered specimen. This made the sample preparation process simpler and more accurate without the risk of contamination. The procedure for sample preparation involved milling of the tailings material to fraction less than 75 µm. The Retsch RS 200 vibratory disk milling machine set at 1500 min⁻¹ motor speed for 5 minutes was used. The milled specimen was obtained in XRF cup and placed in the XRF spectrometer and analyzed for heavy metals concentration.

Determination of contamination parameters

The data obtained from experiment was used to determine the following parameters.

Pollution indicators

The pollution indicators were calculated using Equation 1 and 2.

Enrichment Factor (EF)=[Concentration of Metals in Tin Mine tailing]/[Concentration of Metals in Control site](1)

Geo accumulation index (I-geo)=log 2 [Cn/1.5 × Bn](2)

Where Cn=Concentration of metals in tin mine tailings, Bn=Concentration of metals in control sites.

Attributes	pH	pH	Bulk Density (g/cm3)	Bulk Density (g/cm3)	Electrical conductivity (Ms/m)	Electrical conductivity (Ms/m)
Samples	S1	S2	S1	S2	S1	S2
Tin Mine Tailing	5.31	4.97	2.43	2.47	40	20
Control	6.32	5.71	2.31	2.35	30	10

Table 1: Physicochemical attributes of tin mine tailing and control.

Heavy metal concentration in tin mine tailings and control sites

Energy dispersive X-ray fluorescence spectrometer EDX-XRF (MiniPAL4) was used to determine heavy metal concentration of the Tin mine tailings and the control samples. The heavy metals

Heavy Metal	Tin Mine Tailing	Tin Mine Tailing	Control	Control	USEPA(2009)
	S1	S2	S1	S2	
Pb	300	300	280	270	80
Cr	200	1900	170	1,600	1,00,000
As	80	80	70	60	0.07

1.5 is the background matrix correction factor due to lithogenic effects [10].

Potential ecological risk assessment

Risk index (RI)=ΣEr(3)

Where Σ=Sum of all risk factors, E=Enrichment factor, r=Response risk factor.

Results and Discussion

Physico-chemical attributes of the tin mine tailing and control sites

The physicochemical results are as shown on Table 1. The results of the tin mine tailing pH obtained for S1 and S2 from the mining and control sites were (5.31 and 4.97) and (6.32 and 5.71) respectively. These showed that the mine sites is more acidic than the control sites.

The bulk density for S1 and S2 of the tin mine tailing and the control sites are (2.43 and 2.47 g/cm³) and (2.31 and 2.35 g/cm³) respectively. The lower the bulk density values, the better its ability for regeneration upon use [11]. From the results all are below the permissible limits (6 g/cm³) and effective and suitable for plants growth.

The results of tin mine tailing electrical conductivity obtained for S1 and S2 from the mining and control sites are (40 and 20 Ms/m) and (30 and 10 Ms/m) respectively which are below the permissible limits (100 Ms/m) and so can be effective and suitable for plants growth.

concentration of tin mine tailing and control sites are shown in Table 2. The concentration of the heavy metals were within the maximum permissible limits of soil except for Pb and As in mining and control sites were of range (270-300) mg/kg and (60-80) mg/kg, which are above the permissible limits (80 and 0.07 mg/kg) respectively [12].

Zn	BDL	200	BDL	180	23,000
Cd	BDL	BDL	BDL	BDL	1.7
Ni	80	80	70	70	1,600
BDL: Below detection limits					

Table 2: Heavy metal concentration in tin mine tailings and control samples in (mg/kg).

The research work carried out in aqueous environment [13], the inorganic arsenic species' Arsenite As (III) and Arsenate As (V) are the most abundant species and their transport is aided by competitive adsorption, an alkaline pH and sub-toxic aqueous environment. The high concentration of Arsenic and lead could be attributed to the mining activities, transport mechanism, which includes agricultural activities such as application of agrochemicals and atmospheric depositions on the site. This is in agreement with the work reported by Chen et al. [14].

Similarly, the concentrations of the metals in soil samples obtained from the mining site are significantly higher than their corresponding levels in the control samples. This agreed with the work of Uwah et al. [15], who reported that, the high level of heavy metals in soil is associated with anthropogenic activities. Heavy metals in the soil form anthropogenic sources tend to be more mobile, hence bioavailable than pedogenic, or lithogenic ones [16]. Zn present in the area could be as a result of its natural abundance and its association with Cadmium as a result of mechanical abrasion of crushing/grinding [17]. This study agreed with the report of Banerjee [18], that Zn is associated with Fe-Mn oxide phase because of the high stability constant of Zn oxides. Iron oxides adsorb considerable quantities of Zn, and this oxide may also include Zn in the lattice structure.

Enrichment factor and geo-accumulation

Enrichment factor and Geo accumulation values can be seen on Tables 3 and 4. The Enrichment Factor (EF) and Geo accumulation Factor (I-geo) was calculated for 5 metals (Pb, Cr, As, Ni and Zn) however, Cd and Cu was not calculated due to insignificant concentration of the heavy metals in the tin mine tailings.

Heavy Metal	Enrichment Factor S1	S2
Pb	1.07	1.11
Cr	1.18	1.19
As	1.14	1.33
Ni	1.14	1.14
Cd	ND	ND
Cu	ND	ND
Zn	ND	1.11
ND: Not Detected		

Table 3: Enrichment Factor (EF) of Tin Mine Tailing.

The enrichment factor that was calculated for the 5 metals obtained from the study areas to establish the degree of soil contamination and

heavy metals accumulation. It is the ratio between the concentration of metals in contaminated soil and concentration of metals in uncontaminated (control) soils, in which values greater than 1 indicate environmental pollution [19]. Their respective EF values for S1 are (1.07, 1.18, 1.14, 1.14) for Pb, Cr, As and Ni while S2 are (1.11, 1.19, 1.33, 1.14, 1.11) respectively for Pb, Cr, As, Ni and Zn for the 5 metals studied.

Heavy Metal	I-geo S1	S2
Pb	0.22	0.22
Cr	0.24	0.24
As	0.23	0.27
Ni	0.23	0.23
Cd	ND	ND
Cu	ND	ND
Zn	ND	0.22
ND: Not Detected		

Table 4: Geo-accumulation (I-geo) of tin mine tailing.

The EF values are far above the value of contamination resulting in high availability and distribution of metals in the soils. Their high EF values are attributed to the mining and smelting activities taken place in the study area. These values may be an indication that there may ultimately be an increase in metal accumulation in the soil on the sites [19]. The result of the Enrichment Factor (EF) and Geo accumulation Factor (I-geo) shows that Cd and Cu contaminant is very low or negligible, while Pb and As are the most contaminants, Ni, Zn and Cr are within the permissible limit in the study areas [12].

Scanning electron microscopy characterization of tin mines tailings

To determine the surface morphology of the Tin Mines Tailings, Scanning electron microscope (SEM-MVE016477830) was used. The sputter coater was operated in an argon atmosphere using a current of 6 mA for 3 minutes in an experimental condition [20].

Results of S1 in Plate 1, showed a homogenous small size particles with fine porous structure in nano-scale range. While Plate 2, indicates micrograph for (S2) showing a compact, macro-pores with well-developed tubular crystalline structure. The external surface shows a rough area having different irregular shapes of varying sizes and pore diameters distributed over the surface [21]. From the result it can be concluded that the S2 has more pore than the S1 (Plates 1 and 2).

Previous studies on nano crystalline structure have shown that pure meta stable tetragonal phase can be stabilized which the crystal size is below a critical size primarily due to very low surface energy associated

with it. When the crystal size exceeds this size, the transformation of meta stable phase to monoclinic one occurs due to a decrease in surface energy [21].

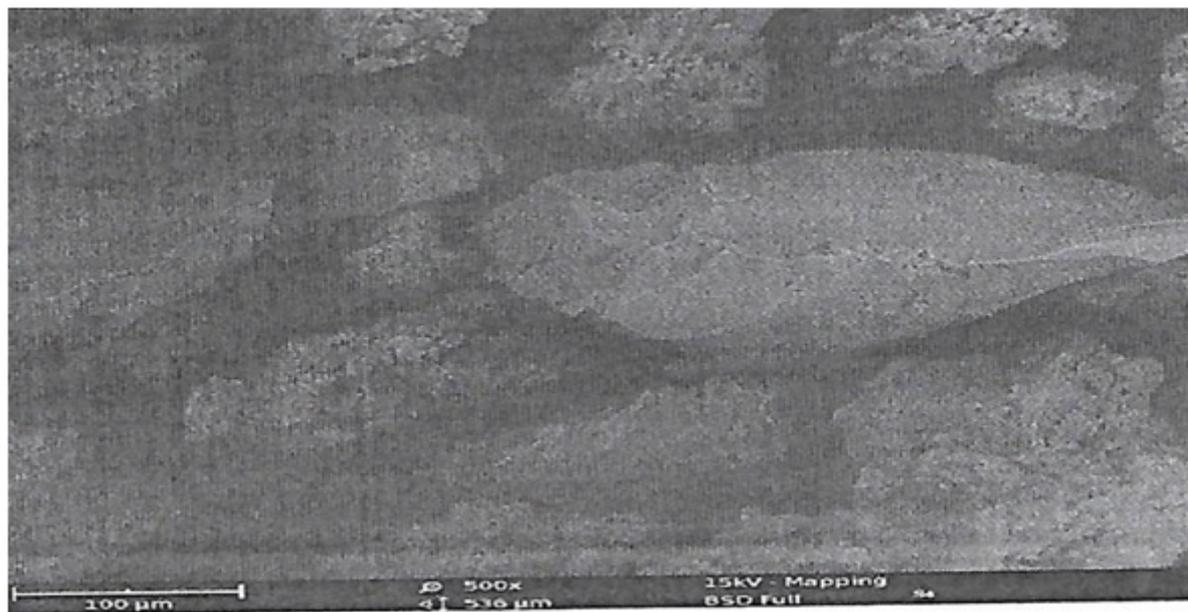


Plate 1: S1: Homogenous small size particles with fine porous structure in nano-scale range.

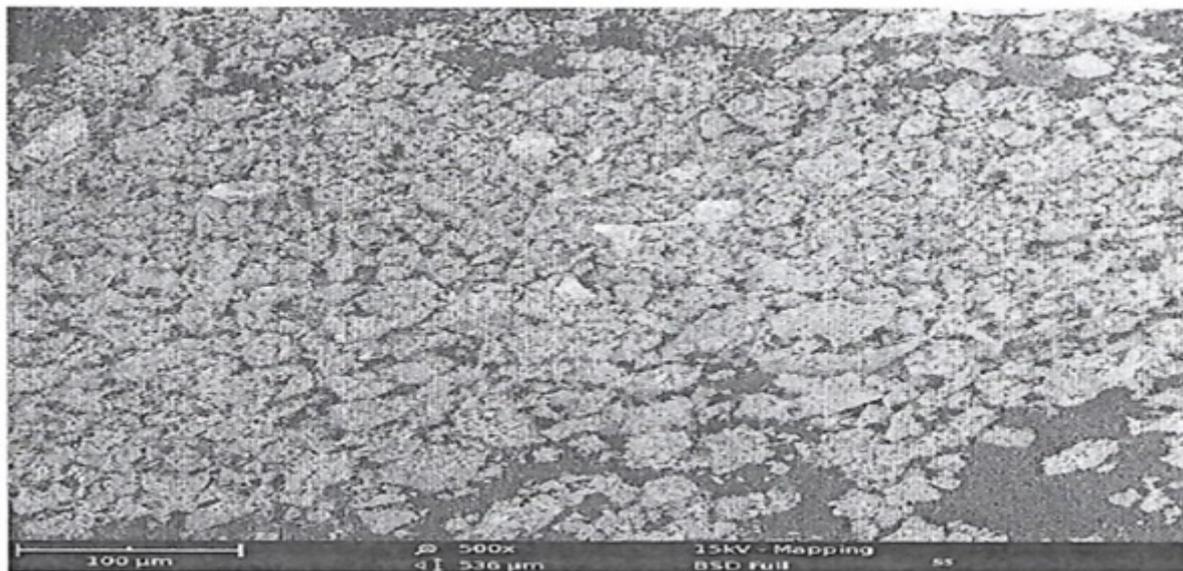


Plate 2: S2: Micrograph for (S2) showing a compact, macro-pores with well-developed tubular crystalline structure.

FTIR for tin mines tailings

Fourier Transform Infra-red (FTIR) (Agilent tech. Cary 360) was used. The FT-IR analysis of samples is shown in Table 5. The FTIR spectrum is important in identification of surface functional groups which plays a great role in adsorption mechanism and capacity [11].

From the FTIR results for S1 in Figure 2, the absorption bands at (779.0, 1038.2 and 2108.7) cm^{-1} indicate the presence of compounds such as Silver Bromate, Calcium Sulphate/Potassium Metaborate and Magnesium perchlorate/sodium chromate respectively. These are as a result of the geochemical composition of the mineral that formed the parent rock of the area [22].

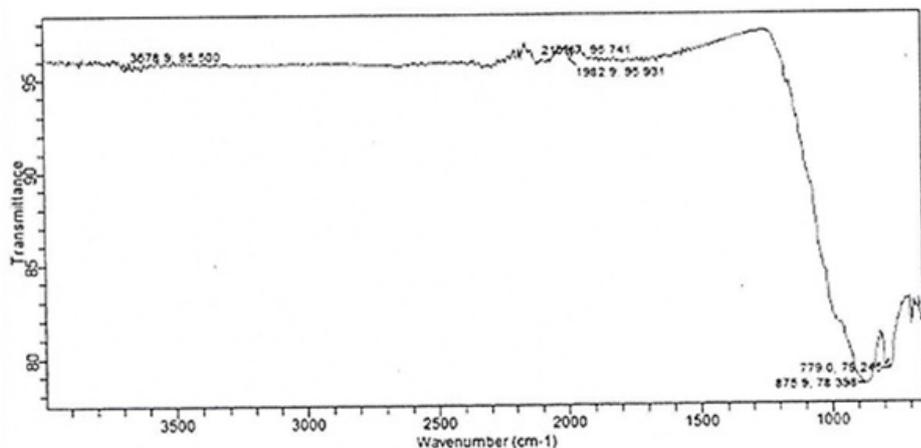


Figure 2: S1 FTIR showing the characteristics spectra peaks.

From the S2 FTIR results in Figure 3, the absorption bands at (2173.0) cm^{-1} indicates magnesium per chlorate and sodium chromate [23].

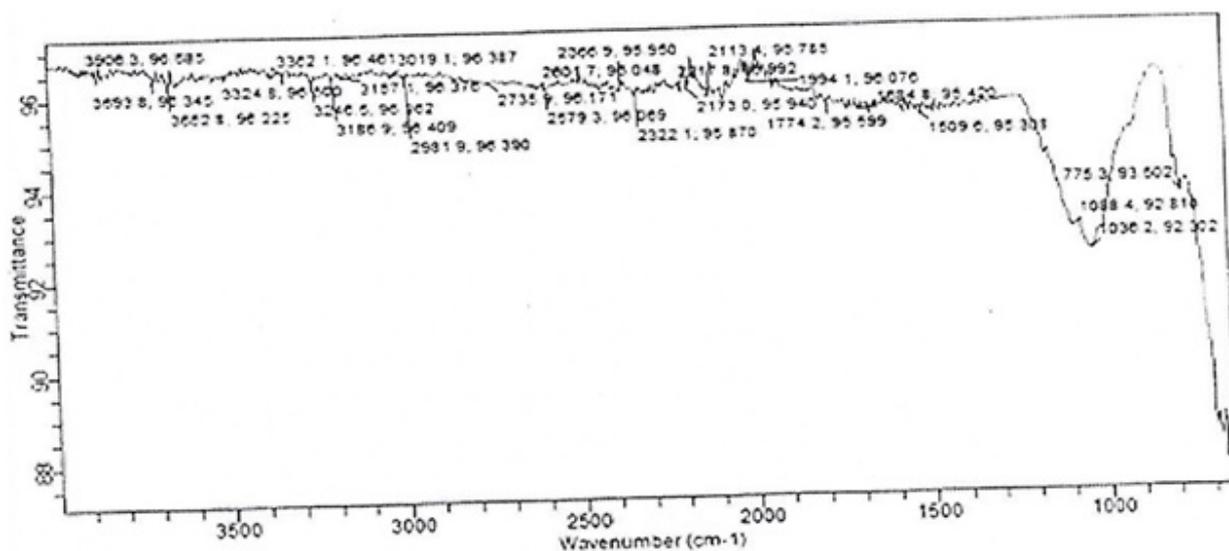


Figure 3: S2 FTIR showing the characteristics spectra peaks.

Group Freq (cm^{-1})	Functional Group	Observed S1	Frequencies S2	Assignment
700-950	Ag^+	779	-	Silver Bromate
1100-1000	$\text{K}^+ \text{Ca}^{2+}$	1038.2	-	Calcium Sulphate and Potassium Metaborate
1000-2200	$\text{Mg}^{2+} \text{Na}^+$	2108.7	2173	Magnesium Per Chlorate, Sodium Chromate

Table 5: FTIR spectral information of tin mine tailings.

Potential ecological risk assessment of heavy metals

According to various reference systems, large difference of Er may occur among the results. The tin mine tailings of Rim, Sharubutu and environs and the control samples are considered as screening levels. The potential ecological risk indices (Er, RI) of heavy metals are shown in Table 6.

Heavy Metal	Er	Er
	S1	S2
Pb	5.35	5.55
As	11.4	13.3
Ni	5.7	5.7
Zn	ND	1.11
Risk Index (RI)	24.81	28.04
ND: Not Detected		

Table 6: Potential ecological risk index of tin mine tailings.

With the use of tin mine tailing value as screening level Er for heavy metals detected for Pb, Cr, As, Ni and Zn were less than 40. The heavy metals Pb, Cr, As, Ni and Zn posed low ecological risk to the ecosystem. Comparison of the value of RI among different heavy metals reveals that the ecological risk of individual heavy metals in the tin mine tailing in the mine site is higher than the control samples. The combined ecological risk of the tin mine tailing is mainly low level, lower than the control samples which poses considerable low risk to the ecosystem [24].

Conclusion

The results of the elemental analysis using Energy dispersive X-ray fluorescence spectrometer EDX-XRF (MiniPAL4) showed that both the mining and control sites in Riyom L.G.A (Rim and Sharubutu) and environs contains certain concentration of heavy metals in different fractions (Pb Ni, Cr, Zn and As) were determined. Mining activities contaminate soil and hence all the samples areas are contaminated as indicated by enrichment factor and geo accumulation factor. The potential ecological risk indices (Er, Ri) of heavy metals in tin mine tailing of the studied areas posed low ecological risk to the ecosystem as indicated by risk index. The surface morphology of the tin mine tailings through the use of Scanning electron microscopy (SEM) technique revealed fully homogeneous small size particles and heterogeneous particles sizes with irregular shapes for both the S1 and S2 respectively. The Fourier transform infrared (FTIR) spectral analysis showed the functionality of Ag, Ca, K, Mg and Na compounds within the band range of 700-2200 cm^{-1} .

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Conflict of Interest

There are no conflict of interest or otherwise.

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