Volume-3, Issue-4, April-2019: 52-59
International Journal of Recent Innovations in Academic Research ISSN: 2635-3040

Heavy Metals Content and Some Physiochemical Parameters of Tailings at an Abandoned Barite Mine Site at Azara, Awe, Nassarawa State, Central Nigeria

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Received: March 30, 2019; **Accepted:** April 6, 2019; **Published:** April 10, 2019

Abstract: Mine tailings are characterized by high concentrations of heavy metals. The direct effects of mining wastes includes loss of agricultural land, forest or grazing land and the release of heavy metals into the environment even after the closure of mine sites. Samples were collected from three sample veins from Azara Barite mining site in Awe Local Government Area, Nasarawa State. Grab tailings samples were collected from the ground surface at the sampling sites. At each site, five random samples were collected and thoroughly mixed to form a composite and representative sample per vein. The physiochemical properties of the tailings samples were obtained. The results are vein 1 (5.3), vein 2 (5.9) and vein 3 (6.9) which shows that the tailings are moderately acidic with vein 1 being most acidic with pH 5.3. The tailings are sandy in nature with highest percentage of 95%, Organic matter content is low which account for low agricultural activities in the area. The tailings heavy metal concentration mg/kg in mine tailings were obtained using Atomic Absorption spectrophotometer and the result shows that, Cd ranged from (244.40-331.92 mg/kg), Cu from (141.52 -390.36 mg/kg), Ni from (130.00-166.00 mg/kg), Pb from (135.05-165.50 mg/kg) and Zn from (331.75-599.73 mg/kg). These concentrations were higher than the permissible limit (mg/kg) set by Nigerian Environmental Standard and Regulation Enforcement Agency (NESREA).

Keywords: mine tailings, heavy metals, Atomic Absorption spectrophotometer, Barite.

Citation: Ogidi A. Ogidi, Alaku Yakubu, Danja, B.A., Sanusi, K.A., Nathaniel Sunday Samuel, Abdurrahman Abubakar and Hammashi H. Lodma. 2019. Heavy Metals Content and Some Physiochemical Parameters of Tailings at an Abandoned Barite Mine Site at Azara, Awe, Nassarawa State, Central Nigeria. International Journal of Recent Innovations in Academic Research, 3(4): 52-59.

1.0 Introduction

The release of large amounts of heavy metals into the environment by anthropogenic activities results in a number of environmental issues. Living organisms require trace amounts of some heavy metals e.g. cobalt, vanadium, strontium and zinc (Kisamo, 2003).

Contamination of soils due to the accumulation of heavy metals through emission from mining sites is one of the risks associated with mining activities.

Heavy metals constitute an ill-defined group of inorganic chemical hazards, and the most commonly present at contaminated sites are, Pb, Cr, As, Zn, Cd, Cu, Hg and Ni (Zhang *et al.*, 2010). Speciation and bioavailability of heavy metals are possible. Heavy metal contamination of soils may pose serious risk and hazards to man and the environment through direct ingestion and contact with contaminated soils, contamination of ground drinking water, reduction in food quality, and land use for agricultural activities (Wuana *et al.*, 2011).

Although the exact composition of tailings is site-specific, they generally contain heavy metals, and radioactive material. Waste rock stockpiles have many of the same problems, and are made out of the same materials, but in coarser mineral form (Beauford, 2012). The primary concern when determining how best to manage waste is preventing water pollution. A water body can be polluted in three different ways, which may occur in isolation or with each other: sedimentation, acid drainage, and metals deposition (Bradsher, 2011). Surface mining operations have the potential to affect flora and fauna, and contaminate soil, air and water in the environments (Marques *et al.*, 2001). Heavy metals are transferred off-site even after the closure of a mine. The direct effects of mining wastes include loss of cultivated land, forest or grazing land, and overall loss of production (Wong, 2003).

Tailings are generally stored on the surface either within retaining structures or in the form of piles (dry stacks) but can also be stored underground in mined out voids by a process commonly referred to as backfill. Backfilling can provide ground and wall support, improve ventilation, provide an alternative to surface tailings storage and prevent subsidence. The process of beneficiation of run of the mine ores and subsequent disposal to surface containment facilities exposes elements to accelerated weathering and can consequently increase their mobilization rates. The addition of reagents used in mineral processing may also change the chemical characteristics of the processed minerals and therefore the properties of the tailings and waste rock (EC, 2004).

Barite occurs in a large number of depositional environments, and is deposited through a large number of processes including biogenic, hydrothermal and evaporation, among others, barite commonly occurs in lead-zinc veins in limestone, in hot spring deposits and with hematite ore. It has also been identified in meteorites (Rubin, 1997). Mining activities have been going on in this locality for many years, although the physical degradation of the environment is noticeable, the effect of heavy metals may not be seen but the danger is real and enormous, hence this study is to determine heavy metals such as Cd, Cu, Fe, Ni, Pb and Zn, and associated with mines tailings and provide information to general public on the threat associated with heavy metals from mine tailings from abandoned mines.

2.0 Materials and Methods`

2.1 Study Area (Description)

Azara is located in Nasarwa state of Nigeria and has an elevation of 224 meters above sea level and its population amounts to 71,657. Its coordinates are 8°22'0" N and 9°15'0"E.

2.2 Sample collection and Pretreatment

Soil samples were collected from three sample veins (A, B and C). Grab soil samples were collected from 15cm below the ground surface from sampling sites using a plastic scoop. Soil samples were collected randomly, air dried at room temperature of 20-30^{o}C. Samples were packed in pre-cleaned, acid treated, airtight plastic bags, transferred to the laboratory for further processing and analyses. In the laboratory, soil samples were air-dried at room temperature, homogenized/gently crushed using an agate mortar and pestle and sieved through a standard sieve of 2 mm mesh size. Soil samples with particle size of <2 mm were stored in acid washed plastic containers. At each site five random samples will be collected and thoroughly mixed to get a composite and representative sample per vein (Tandon, 2001).

2.3 Physicochemical Analysis of Tailings

Some of the physicochemical parameters of the tailing samples were analyzed, they include, pH, CEC, texture, and organic matter.

2.3.1 pH

The pH of soil samples were measured using hand held pH meter. 20g air-dry tailing sample was mixed with 100mL of dilute concentration (0.01M) of calcium chloride ($CaCl_2$) in a 250mL volumetric flask, shaken for an hour and the pH measured (Miller and Kissel, 2010).

2.3.2 Organic Matter Content

The mass of an empty, clean and dry porcelain dish (MP) was determined and recorded. Part of or the entire oven-dried test specimen was placed in the porcelain dish and the mass of the dish and soil sample (MPDS) determined and recorded. The dish was placed in a muffle furnace at a temperature of 440^{o}C and left in the furnace overnight. The porcelain dish was remove carefully using tongs, and allowed to cool to room temperature. The mass of the dish containing the ash (burned soil) (MPA) was Determined and recorded. The organic matter was determined via the following steps (Reddy, 2002).

(1) Determine the mass of the dry soil.
MD=MPDS-MP

(2) Determine the mass of the ashed (burned) soil.
MA=MPA-MP

(3) Determine the mass of organic matter
MO = MD–MA

(4) Determine the organic matter (content).
OM= (MO/MD) x 100

2.3.3 Total Heavy Metals Content

Total heavy metals content was determined using atomic absorption spectrophotometer after acid (HNO_3) digestion. 5g of soil sample was weighed out, placed in a 50 mL volumetric flask, and 10mL concentrated HNO_3 added to it. The flask was covered with a watch glass and heated over water bath at low temperature, after digestion was complete sample was filtered using a filter paper into a 100mL volumetric flask and the solution made up to 100mL using de-ionized water and set aside for total metal determination using Atomic Absorption Spectrophotometer (Ndimele and Jimoh, 2011).

2.4 Quality Assurance/Control and Statistical Treatment of Data

Effective safety measures and quality assurance procedures were employed to ensure reliability of the test results. The chemicals and reagents used were of analytical grades. Glassware and utensils used during the research were properly cleaned. Samples were cautiously handled to minimize the cross-contaminations and reagent blank determination was carried out to correct the instrument readings.

3.0 Result/Discussion

3.1 Tailing pH

The tailing pH for tailings samples from vein 1, 2 and 3 were 5.3, 5.9 and 6.9 and the mean value was 6.0. The result shows that the tailings in Azara barite mine area are acidic, with tailing samples from vein 1 being the most acidic and vein 3 being the least acidic of the sample veins.

The pH of tailings samples in this study were all higher than the value 4.8 at a mine tailing dump in Japan reported by Sasaki *et al.*, (2002), and the maximum value of 5.0 for tailings at Ervedosa mine area in Portugal reported by Favas *et al.*, (2011) but less than the pH value of 10.5 at a gold mine in Zimbabwe reported by Zaranyika and Chirinda (2011), the minimum value of 7.2 and maximum value of 7.6 for tailings at Draa Lasfar mine, Marrakech, Morroco reported by Yassir *et al.*, (2015) and also less than the minimum 7.1 and the maximum 7.9 at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Barkouch *et al.*, (2015).

3.2 Tailing Textural Analysis

The tailing textural analysis results shows that the mean values in the study were; sand 94.0%, silt 3.7% and clay 2.3%. This indicates that the tailing area at Azara barite mines is sandy. The values for sand was greater than the maximum value 90.5%, the % silt less than the minimum value of 18.1%, and the % clay less than the maximum value of 5.5% for tailings at Ervedosa mine area in Portugal reported by Favas *et al.*, (2011), the % sand in this study greater than the maximum value 52.7%, % silt less than the minimum value 25.9% and the % clay less than the minimum value 21.4% at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Barkouch *et al.*, (2015). The % sand in this study is greater than the maximum value 47.2%, % silt less than the minimum value 25.2% and the % clay less than the minimum value 25.7% for tailings at Draa Lasfar mine, Marrakech, Morroco reported by Yassir *et al.*, (2015).

3.3 Organic matter

The result for organic matter analysis for tailings samples in this study shows vein 1 has a value of 4.3%, vein 2 a value of 4.6% and vein 3 a value of 5.3% with a mean value 4.8%. The values in this study are greater than the maximum value of 4.7% at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Esshaimi *et al.*, (2013), the value 3.5% at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Barkouch *et al.*, (2015), greater than the value of 3.7% for tailings at Draa Lasfar mine, Marrakech, Morroco reported by Yassir *et al.*, (2015). The tailings in Azara barite mine area characterized by low productivity of flora and fauna due to the low organic matter content.

Table 1. Descriptive Statistics of Physiochemical Parameters of tailing Samples

Parameters	V1	V2	V3
pH ($CaCl_2$) (%)	5.27	5.91	6.93
Sand (%)	95.0	93.0	93.0
Silt (%)	3.0	4.0	3.0
Clay (%)	2.0	3.0	2.0
Organic matter (%)	4.3	4.7	4.33

Table 2. Descriptive Statistics of Physiochemical Parameters of tailing Samples

Parameters	Average	Std Dev	Min	Max
pH ($CaCl_2$) (%)	6.0	0.8	5.2	6.9
Sand (%)	94.0	1.0	93.0	95.0
Silt (%)	3.7	0.6	3.0	4.0
Clay (%)	2.3	0.6	2.0	3.0
Organic matter (%)	4.8	0.5	4.33	5.3

3.4 Total heavy metals content

The total heavy metals content of tailings samples were analyzed for Cd, Cu, Fe, Ni, Pb and Zn the concentration values are presented in table 3 and table 4.

Cd

Tailing sample from vein 2 had the maximum concentration of Cd (129.52 mg/kg) and vein 1 had the minimum value (ND) with a mean of 67.70 mg/kg. The values in this study was greater than the maximum value of 6.05 mg/Kg for tailings at Ervedosa mine area in Portugal reported by Favas *et al.*, (2011), 2.82 mg/kg for tailings at Akara gold mine in Thailand reported by Chunhacherdchai *et al.*, (2011), the maximum value of 17.6 mg/Kg for tailings at a gold mine in Zimbabwe reported by Zaranyika and Chirinda (2011), but less than the minimum 4,514 mg/kg for tailings at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Esshaimi *et al.*, (2013), the value 143.1 mg/Kg and for tailings at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Barkouch *et al.*, (2015).

Cu

Tailing sample from vein 2 had the maximum concentration of Cu (390.36 mg/kg) and vein 3 had the minimum value (141.52 mg/Kg) with a mean of 238.42 mg/kg greater than the maximum value of 261.0 mg/Kg for tailings at Ervedosa mine area in Portugal reported by Favas *et al.*, (2011), 6.98 mg/kg for tailings at Akara gold mine in Thailand reported by Chunhacherdchai *et al.*, (2011), but less than the minimum value of 525.0 mg/Kg for tailings at a gold mine in Zimbabwe reported by Zaranyika and Chirinda (2011), 12,760 mg/kg for tailings at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Esshaimi *et al.*, (2013), the value 947.8 mg/Kg and for tailings at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Barkouch *et al.*, (2015) and 971.2 mg/Kg for tailings at Draa Lasfar mine, Marrakech, Morroco reported by Yassir *et al.*, (2015).

Fe

Tailing sample from vein 1 had the maximum concentration of Fe (155,137.7 mg/kg) and vein 2 had the minimum value (80,302.87mg/Kg) with a mean of 107,206.88 mg/kg greater than the maximum value of 4.19 mg/Kg for tailings at Ervedosa mine area in Portugal reported by Favas *et al.*, (2011), 3500.0 mg/kg for tailings at a gold mine in Zimbabwe reported by Zaranyika and Chirinda (2011).

Ni

Tailing sample from vein 1 had the maximum concentration of Ni (166.01 mg/kg) and vein 2 had the minimum value (13.70 mg/Kg) with a mean of 64.26 mg/kg greater than the maximum value of 85.0 mg/Kg for tailings at Ervedosa mine area in Portugal reported by Favas *et al.*, (2011), 75.0 mg/kg for tailings at a gold mine in Zimbabwe reported by Zaranyika and Chirinda (2011), and 44.7 mg/Kg in heavy metal contaminated tailings at a minning area of Barraxiutta, SW of Sardinia, Italy reported by Montinaro *et al.*, (2016).

Pb

Tailing sample from vein 3 had the maximum concentration of Pb (65.50mg/kg) and vein 2 had the minimum value (ND) with a mean of 48.43 mg/kg greater than the minimum value of 29.1 mg/Kg but less than 108 mg/Kg for tailings at Ervedosa mine area in Portugal reported by Favas *et al.*, (2011), 2.83 mg/kg for tailings at Akara gold mine in Thailand reported by Chunhacherdchai et al., (2011), but less than the minimum value of 512.0 mg/Kg for tailings at a gold mine in Zimbabwe reported by Zaranyika and Chirinda (2011).

Zn

Tailing sample from vein 1 had the maximum concentration of Cu (199.73 mg/kg) and vein 3 had the minimum value (31.33 mg/Kg) with a mean of 127.97mg/kg greater than the maximum value of 167.0 mg/Kg for tailings at Ervedosa mine area in Portugal reported by Favas *et al.*, (2011), 30.81 mg/kg for tailings at Akara gold mine in Thailand reported by Chunhacherdchai *et al.*, (2011), 100.0 mg/Kg for tailings at a gold mine in Zimbabwe reported by Zaranyika and Chirinda (2011), but less than the minimum value of 1,804571 mg/kg for tailings at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Esshaimi *et al.*, (2013), the value 3648.0 mg/Kg and for tailings at Sidi Bou Othmane abandoned mine, Marrakech, Morroco reported by Barkouch *et al.*, (2015) and 2123.7 mg/Kg for tailings at Draa Lasfar mine, Marrakech, Morroco reported by Yassir *et al.*, (2015).

Table 3. Total Metal Concentration (mg/Kg) of tailing samples

Metals	V1	V2	V3
Cd	ND	129.52	5.88
Cu	183.39	390.36	141.52
Fe	155,137.7	80,302.87	86,180.08
Ni	166.01	13.08	13.70
Pb	31.35	ND	65.50
Zn	199.73	152.85	31.33
V1= vein one, V2= vein two and V3= vein three			

4.0 Conclusion/Recommendations

4.1 Conclusion

Environmental pollution by heavy metals originating from abandoned mines can become a very important source of contamination both in soil and water. Therefore, the characterization of tailings chemical and physical properties is important to assess the risk of potential environmental mobility of toxic trace metals that are contained in this kind of waste.

The result shows that the tailings in Azara barite mine area are moderately acidic, with tailing samples from vein 1 being the most acidic (5.3) and vein 3 being the least acidic (6.9) of the sample veins. The mean values in the study were sand 94.0%, silt 3.7% and clay 2.3%.

The results indicate that the tailing area at Azara barite mines is sandy. The result for organic matter analysis for tailings samples in this study shows vein 1 has a value of 4.3%, vein 2 a value of 4.6% and vein 3 a value of 5.3% with a mean value 4.8%, this is responsible for the low agricultural productivity around the study area.

The total metal content of tailing samples for heavy metals were above the permissible limits set by DPR, FEBA and WHO metals of concern to human health are Cd, Cr Ni and Pb. Fe has the highest concentration value and Cd the least concentration.

4.2 Recommendations

There is need to monitor mining activities and operations by the government agencies to ensure proper disposal waste during mining operations and also monitor agricultural activities that are carried out around area with active or abandoned mines. There is also need to employ activities and processes capable of reducing excessive heavy metals contents in surrounding soil such as phyto-remediation or chemical washing techniques. The content of heavy metals in ground water around mine site needs to be monitored to avoid health complications due to consumption by humans or animals.

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