

Iron Ore Deposit and Its Tailing Impact on the Toxic Metal Level of Neighboring Agricultural Soils

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AUI and ISE designed, wrote the protocol of the study and managed the analyses. Authors LAE and AAA managed the literature searches, performed the statistical analysis and wrote the first draft of the manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Aim: This is one of our mineralogical study series aimed at the preliminary characterization of iron ore and its neighboring farmland soils, with focus on ore impact on soil quality, toxic metals concentration and the geo-accumulation status of pollutants.

Methodology: Mineral (Iron ore) samples and ore rich soils from neighboring farmlands, coded as I-Soil, I-soil-FLA, I-soil-FLB and I-soil-FLC were collected from Itakpe, Kogi State in North Central Nigeria. Samples were qualitatively characterized using Fourier Transform Infrared Spectrometer (FTIR), Scanning Electron Microscope (SEM) and Ultraviolet Visible (UV-Vis) spectrometer for functional group analysis, micro-structural morphology and spectral profile respectively. Physico-chemical parameters were investigated following routine classical (wet) chemistry procedures. Levels of toxic metals including Iron (Fe), Lead (Pb), Manganese (Mn), Cadmium(Cd), Chromium (Cr), Zinc (Zn), Nickel (Ni) and Copper(Cu) in both ores and soils were estimated using Atomic Adsorption Spectrophotometer (AAS).

Results: The iron ore SEM images appeared compact with irregular shapes. UV –Visible Spectral shows that the mineral has possibly leached from the parent ore to the nearby soils at similar

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range. Highlights of this studies shows that the level of metals in farmland soils are statistically significant ($p < 0.05$) when compared with those of the mineral ores, and insignificant ($p > 0.05$) when compared to acceptable or threshold limits provided by the USEPA and WHO. Relying on geo-accumulation index values, this study classified the farmland soil with regards to the iron load as “extremely contaminated”. Investigated soil samples are “strongly contaminated” with Pb, “moderately contaminated” with Mn and Zn and “uncontaminated” with Cd and Cu.

Conclusion: The parametric factors of the soil samples, soil quality and metal distribution among ore-rich soils showed levels that could be linked to both geogenic and anthropogenic activities. Furthermore, the farmland soil’s toxic metal levels in the study area might be enriched by either mine tailing from the mineral ore depot or anthropogenic. Our recommendation is strictly on continuous environmental impact assessment, environmental monitoring, environmental auditing and environmental awareness campaign.

Keywords: Geo-accumulation; iron ore; soil; contamination; heavy metals; characterization.

1. INTRODUCTION

Environmental contamination because of man’s increasing activities has increased considerably in the past century due mainly to significant increases in industrialization and economic activities. It has been discovered that heavy metals are mainly from the activities of man which can build up in the soil [1]. Sector of mining is one of the ways in which heavy metals are introduced into the surrounding of industries. Other air contaminants are introduced with nitrogen oxides and sulfur dioxide including dropping behind much slag, waste tailings and acid drainage. Contact with toxic metals such as, asbestos and silica can happen when milling and mining activities. Ore fragments, mining leachates and mine tailings are discharged right into depressions that are natural, with wetlands sites causing composition concentration that is high [2].

Toxic metals are continuous pollutants in our surrounding that are dangerous to both man and the environment. The sources can be anthropogenic and natural [3,4]. Some toxic metals such as Fe, Cu and Zn are important to the body of organisms; while others like As, Pb, Cd, Hg are not important and have no use biologically [5,6]. When the concentrations are on the increase, important minerals are harmful [7,8].

Soil, polluted by heavy metals can be dangerous to ecosystem and humans by direct intake and contact with pollutant in the food chain, intake of polluted ground water, low quality of food through phyto-toxicity, food insecurity due to decrease land use for agriculture and the problem of land tenure system [9,10]. Changes in their chemical forms (speciation) and bioavailability are,

however, possible. The buildup of toxic minerals and metalloids can contaminate the Soil by the release of pollutants from the growing industries, disposal of wastewater irrigation metal wastes, animal manures, mine tailings, coal combustion residues paints and leaded gasoline, land application of fertilizers, sewage sludge, pesticides, atmospheric deposition and spillage of petrochemicals [11,12]. The soils are usually the highest carrier of toxic metals when introduced to the surrounding by anthropogenic activities that are mentioned above.

Nigeria is rich in different kinds of mineral ores ranging from metallic, fossil fuels, non-metallic and radio-active minerals [13] with different types starting from different kinds of stones. These metals are under exploited when compared to the nation’s deposits. Among other minerals, Nigeria is endowed with many iron ore deposits of which some of them have been investigated and some are still under investigation. The main raw material in iron and steel industries is iron ore. More than three billion tons of these minerals are found in Kogi, Niger, Enugu, Kaduna and Zamfara states, Nigeria. Itakpe in Kogi state is currently known for iron mine [14].

The danger that toxic metals cause to the health of man – involving cadmium, lead and mercury has been studied and well documented [15,16,17]. Relatively efficient mining activities cause plenty waste, release to water and atmosphere, and a report of surrounding pollution in closely communities and environment was reported [18]. We hope that the present study will provide a novel platform to survey and characterize certain minerals for their micro structural morphology, functional group and spectra profile as well as estimate heavy metal contents and transport of the mineral to regions

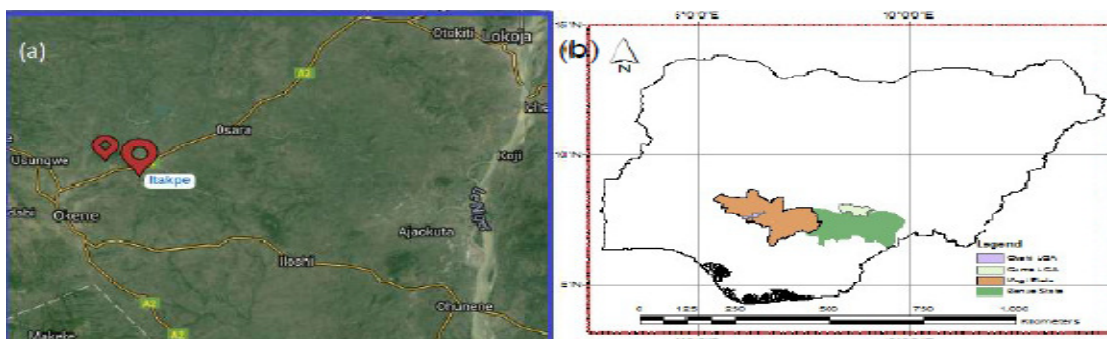


Fig. 1. Google earth image of (a) Itakpe and (b) Nigeria Map showing sampling site (Brown portion)

Source: Google earth image, 2016

near deposit areas, and the possible effects it has on the soil around the farm lands near the ore vicinity.

In addition, practical baseline information on concentration level of eight heavy metals (Pb, Ni, As, Cr, Cd, Fe, Zn and Cu) in the ore location as well as the characteristics of the minerals and possible explanation on its leaching or release were investigated.

In designing the protocol of this study, the hypothesis was that there will be a high metal loading in the mineral deposit region or agricultural farmland, soil, dust, vegetation and water at a level above natural concentrations. In view of this, we investigated mineral (iron ore) characteristics, estimated the levels of heavy metals in farmland soils and ore samples from mineral deposit region in Itakpe, Nigeria and interpreted soil contamination level based on geochemical index to unveil the role played by possible mine tailing and anthropogenic.

1.1 Study Location and Site Description

The study area (Fig. 1) is iron ore depot of the Nigeria iron ore mining company, Itakpe in Okehi LGA of Kogi State and Farmlands coded I-Soil, FLA, FLB and FLC located within the Lokoja–Okene geological area in North Central Nigeria. Itakpe coordinate are as follows: longitude 6°16'E and latitude 7°36'N. Mining activities began in late 70s and beneficiation in early 1990s. The mine suspended production in 2008 without any treatment on the mine waste. Mining sites are characterized by dust laden metals spread on every surface in the area and linked to blasting of the ore during mining with deposited concentration on near agricultural soils, water and plants depending on distance from the mine

and the mode of transport. Thus, tailings and wastes are distributed by wind and erosion on soils, plants and water in the near vicinity of the mine site. It was documented that Itakpe environs is seen as crystalline basement complex with compositional variability and structural complexity covering over 7,770 square kilometers [19] and with sedimentary features of sand stones and mud rocks of cretaceous to tertiary age covering about one third of the area [20]. Tropical climate with 6 months (May to October) of rainy season and 6 months (November–April) dry season is the most probable description of the study area. Majority of the inhabitants of Itakpe are engaged in subsistence agriculture.

2. MATERIALS AND METHODS

2.1 Sampling

Table 1 shows the mineral ore, farmland soils (FLA, B and C) and control samples with their respective codes.

2.1.1 Sampling of the ores

Twenty mineral ore samples were handpicked randomly from the ore depots in the month of January, 2016 using technical aid assistance by technical staff from the Nigeria iron ore mining company, Itakpe. Samples were stored in a nitric acid pre-treated dry polypropylene bag, labeled and taken to the laboratory and stored under ambient condition [21].

2.1.2 Sampling of the soil

Documented soil sampling techniques [21,22] were adopted. Four top soil samples from 0–15 cm of each location were randomly collected by

scooping surface soil of the sampling areas (east, west, north and south) using a stainless steel hand trowel, also four soil samples were randomly collected each from three different farm land within the vicinity of both sites A,B and C. Sixteen soil samples (four from each location) were stored in a nitric acid pre-treated and dry polypropylene bags and were well labeled as I-soil, I-Soil-FLA, I-soil-FLB and I-soil-FLC (Table 1) and taken to the laboratory and stored under ambient condition prior to analysis. Samples were homogenized and representative samples were taken for analysis.

2.1.3 Soil sampling for control experiment

Four top soil samples outside mineral depot region (1000 m away from the mining areas and from north, south, east and west of the farmland) coded as I-Ref-Soil or non iron soil (NI-Soil) was taken as control, all the samples collected were stored under ambient condition [21,22].

In this study, physico-chemical parameters (pH, bulk density, conductivity, moisture content and particle size) were investigated using routine classical analytical methods. Adopted for functional group analysis is spectrum recorded on an Agilent technologies Cary 630 Fourier Transform Infrared Spectrometer. To characterize the ores samples for their micro structural morphology a Phenomenon MVE016477830 Scanning Electron Microscope (SEM) was used. Spectrophotometer was used to study the spectral profile of the ores while Atomic absorption Spectrophotometer (AAS) (Varian AA240FS) was used to estimate the concentration of heavy metals. Metal distribution and soil contamination factor by heavy metal were predicted by computation. Analytical grade reagents were used throughout the study.

2.2 Preparation of Stock and Standard Solutions

Stock and standard solution including metal stocks (1000 ppm Iron, Lead, Manganese, Zinc, Chromium, Cadmium, Nickel, Copper solution and other routine bench reagents were prepared following standard laboratory procedures.

2.3 Preparation of Soil Sample

Methods from two reports [22,23] were adopted. Soil samples were manually sorted to remove pebbles and coarse materials, and were air-dried under ambient conditions in the laboratory for

seventy-two hours. The dried soil samples were passed through a 2 mm sieve to eliminate coarse particles; the soil samples were ground to fine powder in a disc mill crusher in preparation for analysis.

2.4 Physicochemical Parameters

2.4.1 pH measurement

pH was analyzed using standard method [23]. Mixture of soil and distilled water 1:1, w/v was prepared by weighing 20 g of fine grained soil into a glass beaker and 20 mL of de-ionized distilled water was added to each beaker and stirred gently to enhance H⁺ (Hydrogen ions) release from soil. The pH was determined after the mixtures were allowed to stand for 30 minutes using a pH meter.

2.4.2 Particle size analysis

Bouyoucos Hydrometer Method [24] was used to determine the particle size of the samples. 50 g of air dried samples which has been passed through a 2-mm sieve was transferred to a "milkshake" mix cup. 50 mL of Calgon (7 g Sodium carbonate and 50 g sodium hexametaphosphate) was mixed to make a liter with distilled water) was then added. The mixture was stirred with a stirring rod and allowed to settle for 30 minutes. At the end of 30th minute, the suspension was again stirred for 15 minutes with the multimix machine. The suspension was then transferred from the cup to the graduated glass cylinder (1500 mL). With hydrometer in suspension; distilled water was then added to give a total volume of 1130 mL. The hydrometer was then removed. The top of the cylinder was covered and steadied with the hand and inverted several times until all sample soil and ore was in suspension. The cylinder was place on a flat surface and the noted. The hydrometer was immediately placed into suspension sliding it slowly until floating. The first hydrometer reading, H₁, was taken at 40 seconds after the cylinder was set down. The hydrometer was then removed and the temperature, T₁, of the suspension was recorded with the thermometer. The suspension stood for further 3 hours and the second hydrometer H₂, reading was taken, as well as the temperature T₂. The first reading measured the percentage of the silk and clay in suspension, whereas the second reading indicates the percentage of total clay in the suspension.

Table 1. Sample codes of iron ores and soils from neighboring farmland

S/No	Sample Codes	Description
1	Iron Ore	Iron ore from Itakpe, Kogi State
2	I-Soil	Soil samples around Iron ore depot
3	I-Soil-FLA	Iron ore contaminated soil from Farmland A
4	I-Soil-FLB	Iron ore contaminated soil from Farmland B
5	I-Soil-FLC	Iron ore contaminated soil from Farmland C
6	I-Ref-Soil	Control Soil samples from non Iron ore rich Farmland

The result were corrected to a temperature of 20°C, a 0.2 reading was added to hydrometer reading before the computation and every degree below 20°C, 0.2 reading was subtracted from hydrometer reading. In addition, 2.0 reading was subtracted from every hydrometer reading to compensate for the added dispersing agent. Soil particle sizes were computed as shown in equations 1-3 [24].

$$\% \text{ Sand} = 100.0 - [H_1 + 0.2(T_1 - 20) - 2.0]2 \quad (1)$$

$$\% \text{ Clay} = [H_2 + 0.2(T_2 - 20) - 2.0] \quad (2)$$

$$\% \text{ Silk} = 100.0 - (\% \text{ sand} + \% \text{ clay}) \quad (3)$$

where H_1 is hydrometer reading at 40 seconds, T_1 is temperature at 40 seconds, H_2 is hydrometer reading at 3 hours, T_2 is temperature reading at 3 hours, temperature correction to be added to hydrometer reading = 0.2 (T-20), where T is in degrees Fahrenheit.

2.4.3 Bulk density

The soil sample was filled into 100 mL measuring cylinder to a given volume. The cylinder was tapped for at least 2 minutes to compact the Soil and then weighed. The bulk density was calculated [25].

$$\text{Bulk density} = \frac{\text{Sample mass (g)}}{\text{Vol. of packed sample (cm}^3\text{)}} \quad (4)$$

2.4.4 Conductivity measurement

each soil sample (10 g) was weighed into 100 mL beakers, 20 mL of distilled water was added to the soil and allowed to settle for 30 minutes, the mixture was filtered using Whatman filter paper. The electrode was immersed into the soil solution and conductivity reading of each sample was recorded [26].

2.4.5 Moisture content

The fine soil samples (5 g) were transferred into a tarred moisture tin and weighed dried over

night at 105°C (lid removed).The tin was removed from oven, and close with lid, it was then cool in desiccators and weighed [27].

The moisture content in wt% (w/w) was obtained using equation 5.

$$\text{Moist wt \%} = \frac{A - B}{B - \text{tared tin}} \times 100 \quad (5)$$

where A and B represents wet and oven dried soil respectively.

2.5 Digestion of Soil and Mineral Ore Samples

2.5.1 Digestion of soil samples

According to the methods documented elsewhere [22,27], 10 g each of the fine grained soil sample was weighed into 250 mL teflons beakers earlier treated by soaking in dilute nitric acid (0.001 M) overnight and dried in oven at 50°C. 10 mL nitric acid and 30 mL hydrochloric acid, HCl analytical grade reagent was added to each beaker and heated in boiling water in a water bath for two hours. The resulting digests was filtered into 50 mL volumetric flasks and made up to 50 mL mark with distilled water. Procedural blank was prepared by heating 15 mL (2 M) nitric acid in 50 mL distilled water for two hours, filtered and made up to 100 mL mark with distilled water.

2.6 Instrumental Analysis

2.6.1 Metal characterization using AAS

The digested sample solutions of soil and mineral ore in 50 mL volumetric flasks was quantified for heavy metals; Cadmium (Cd), Chromium (Cr), Manganese (Mn), Nickel (Ni), Iron (Fe), Zinc (Zn), Lead (Pb) and Copper (Cu) by use of flame Atomic Absorption Spectrometry (FAAS Varian AA240FS). The instrument was set according to the manufacturer's instruction

which determines the present of metals in both mineral and soil digest samples. The sample solution was aspirated into the flame and absorbance was recorded for each element [28].

2.6.2 Characterization of minerals using FTIR

FT-IR measurements were recorded on FTIR model Agilent technologies. Spectrometer in the region of 400-4000 cm⁻¹ supplied with OMNIC software [29].

2.6.3 Characterization of mineral using SEM

The mineral samples were microscopically characterized by the use of Scanning Electron Microscopy (SEM).

2.6.4 Spectral profile determination using UV-Visible

Minimum of 1 g of the fine ground samples (Iron Ore and Soil samples) was weighed into 100 mL beakers, and 2 mL of 11.81 conc. of HCl was added and further diluted with 25 mL of deionised water and filtered using Whatman no.1 filter paper. The blank was prepared by diluting 1 mL of 11.81 M of HCl with 25 mL of deionised water [30]. Sample solution collected into the sample cell was scanned at the UV-Visible range for the absorbance maximum.

2.7 Pollution Load Index (PLI)

The level of metal contamination and distribution was assessed using the geo-accumulation Index (I_{geo}) method [31]. In this model, the status of heavy metal concentration is compared with the background values. This index describes the relationship between the measured metal in the ore fraction and the geochemical value in farmland soil [32].

$$I_{geo} = \log \left[\frac{C_n}{1.5B_n} \right] \tag{6}$$

C_n is the measured concentration of the soil and B_n is the geochemical background value. The constant, 1.5, stands for background matrix correction factor linked to lithological variations [31,32].

2.8 Comparative Study (Statistical Treatment of Data)

The data thus obtained was and subjected to statistical analysis of variance (ANOVA) via the

student t-test. Test of significance was set at 95% confidence level. Description statistics for each parameter was based on mean and standard deviations of triplicate analysis. The mean values were compared with results of similar studies in Nigeria and other countries including their allowable permissible limits [33,34].

3. RESULTS AND DISCUSSION

3.1 Physical Examination of Sample

Fig. 2 is a photograph showing mineral ores and soils from farmlands around their vicinities. Iron Ore appeared rocky, I-Soil, I-Soil-FLA, I-Soil-FLB and I-Soil-FLC appears lumpy while I-Ref-Soil looks more of the sandy sand.



Fig. 2. (a) Iron Ore, (b-e) Soils from Itakpe and (f) control soil sample

3.2 Physicochemical Parameters

Physicochemical parameters of mineral Ores and there corresponding soil samples namely: pH, Conductivity, Bulk density, Moisture content and Particle size are represented in Table 2.

3.2.1 pH of iron ore and soil sample

The pH of Iron ore and all the soil samples analyzed range from 6.67 to 6.98, with highest value in iron ore. This is in good agreement with the pH value reported as 7.01 to 7.99 [35]. pH is an important soil property, having great effects on solute concentration and absorption in soil. The acidic pH levels tend to have an increased micronutrient solubility and mobility as well as increased heavy metal concentration in the soil. These are however, in neutral boundary.

Table 2. Physicochemical characteristics of iron ore and soil samples from Itakpe

Samples	Parameters			
	pH	Conductivity ($\mu\text{S.cm}^{-1}$)	Bulk density (g.cm^{-3})	Moisture content (%)
Iron Ore	6.98 \pm 0.0003	260 \pm 0.3300	3.08 \pm 0.0003	8.50 \pm 0.0130
I-Soil	6.67 \pm 0.0001	352 \pm 3.0000	2.10 \pm 0.0003	15.6 \pm 0.0300
I-Soil-FLA	6.84 \pm 0.0003	453 \pm 1.3300	1.26 \pm 0.0003	27.7 \pm 0.1300
I-Soil-FLB	6.76 \pm 0.0003	394 \pm 3.0000	1.35 \pm 0.0001	25.4 \pm 0.0130
I-Soil-FLC	6.67 \pm 0.0050	447 \pm 3.0000	1.22 \pm 0.0004	29.0 \pm 0.0130
I-Ref-Soil	6.92 \pm 0.0010	309 \pm 1.3300	1.74 \pm 0.0001	17.7 \pm 0.0130

3.2.2 Conductivity measurement of iron ore and soil samples

Results of conductivity measurements range from 260 to 453 $\mu\text{S.cm}^{-1}$. The highest value was found in farmland A (453 $\mu\text{S.cm}^{-1}$) while the least value was in Iron. The conductivity measurement of 165 - 210 $\mu\text{S.cm}^{-1}$ which was previously reported [35] was lower than result reported in the present study. The increase in conductivity may be due to increase in the concentration of some soluble salt in the soil [35].

3.2.3 Bulk density of iron ore and soil samples

The bulk density of Iron ore and soil samples range between 1.22 g.cm^{-3} in I-Soil-FLC to 3.08 in Iron ore. Similar work [36] gave the bulk density ranging from 2.0 to 3.12 g.cm^{-3} . The bulk density reported in the present study fall within the range reported in literature [36]. High bulk density ($> 1.5 \text{g.cm}^{-3}$) reduces water infiltration and plant root penetration resulting in increase in surface water pollution [37]. It is also widely believed that soil BD declines with an increase in soil organic matter because of the increase in porosity volume [38].

3.2.4 Moisture content

The moisture content of Iron ore and soil samples range between 8.5% of Iron ore to 29.2 in I-Soil-FLC. The highest mean was shown in I-Soil-FLC, followed by 27.7% (I-Soil-FLA), 25.4% (I-Soil-FLB), 17.7% (control), 15.5 (I-soil) and the list moisture content was found in Iron

to be 8.5%. The average moisture content of 5% was found to be sufficient for plant growth [39].

3.2.5 Particle size of soil samples from iron rich soil region

The result of particle size (Table 3) revealed a higher value of sand ranging from 58.64 to 76.63%, followed by clay, which ranges from 14.07 to 24.73% and silt ranged from 9.28 to 15.27% [40] reported on soil particle size of sand 8.40 to 91.42%, clay from 5.46 to 6.48% and silt from 9.28% to 15.27%. According to literature [41], soil that has separate increase sand and small clay content has increase pollutant leaching ability. Though Itakpe soil predominantly has high sand fraction ($>77.0\%$) that permits the increase permeability of water and leachates, the textural class (loamy sand) can be good for sanitary landfills [42]. The control sites soil consisted of average high clay fractions thus can exhibit plasticity and allows surface water flooding and contamination. The control clayed texture also encourages low permeability of water and leachates.

3.3 Scanning Electron Microscopy (SEM)

Characterization of the mineral Ores was also carried out using Scanning Electron Microscopy to determine the surface morphology of the particles. Iron Ore the images appear compact with irregular shape (Fig. 3), unlike an observed image [43] which has irregular, bulkier and agglomerated particles. Leaching metals may result after weathering or blasting of ore.

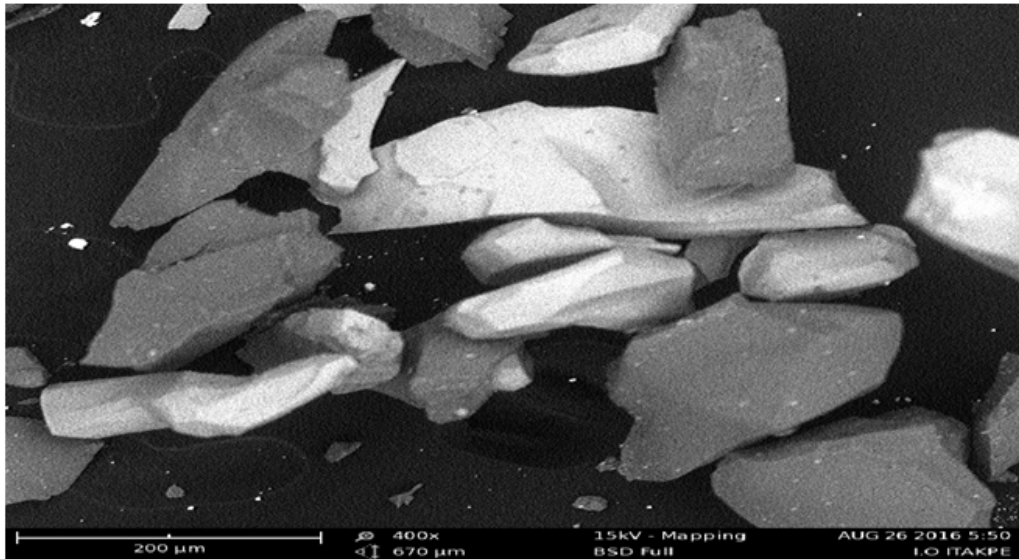
Table 3. Particle size of soil samples from Itakpe iron ore rich region parameters

Samples	Silt (%)	Clay (%)	Sand (%)
I-Soil	14.01 \pm 0.0003	20.07 \pm 0.0001	65.92 \pm 0.0003
I-Soil-FLA	10.01 \pm 0.0001	18.64 \pm 0.0001	71.35 \pm 0.0005
I-Soil-FLB	12.55 \pm 0.0003	22.07 \pm 0.0003	65.35 \pm 0.0001
I-Soil-FLC	15.27 \pm 0.0001	24.73 \pm 0.9400	58.64 \pm 0.0003
I-Ref-Soil	9.280 \pm 0.0001	14.07 \pm 0.0001	76.63 \pm 0.0001

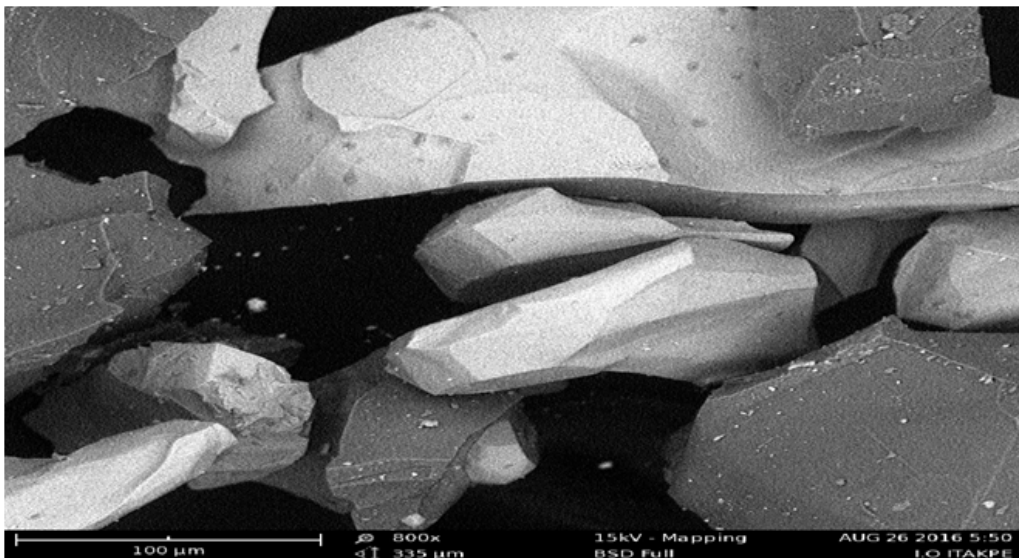
3.4 Fourier Transform Infra-red (FT-IR) Spectroscopic Study

FTIR analytical data (Table 4) is typical of interpretations of spectra shown as Fig. 4. FTIR Characterization was carried out to determine the molecular interaction(s) and functional groups of the mineral ores. Different intensity peak values were recorded to

enable easy identification of the functional groups involved. Peaks were observed at $2322-2005\text{ cm}^{-1}$, $2087-1880\text{ cm}^{-1}$, $1982-1029\text{ cm}^{-1}$, $913-910\text{ cm}^{-1}$, $893-882\text{ cm}^{-1}$ and $798-753\text{ cm}^{-1}$, which confirms that HPO_4 ion, CN ion, Si-O ion, Si-O ion, CO_3 ion and Si-O quartz were active and this may be as a result of NaHPOH_2O , $\text{K}_3\text{Fe}(\text{CN})$, SiO_2 , BaSO_3 , K_2CO_3 and SiO_2 assignment.



a



b

Fig. 3. SEM micrographs of iron ore samples recorded at (a) 400x (b) 800x magnifications

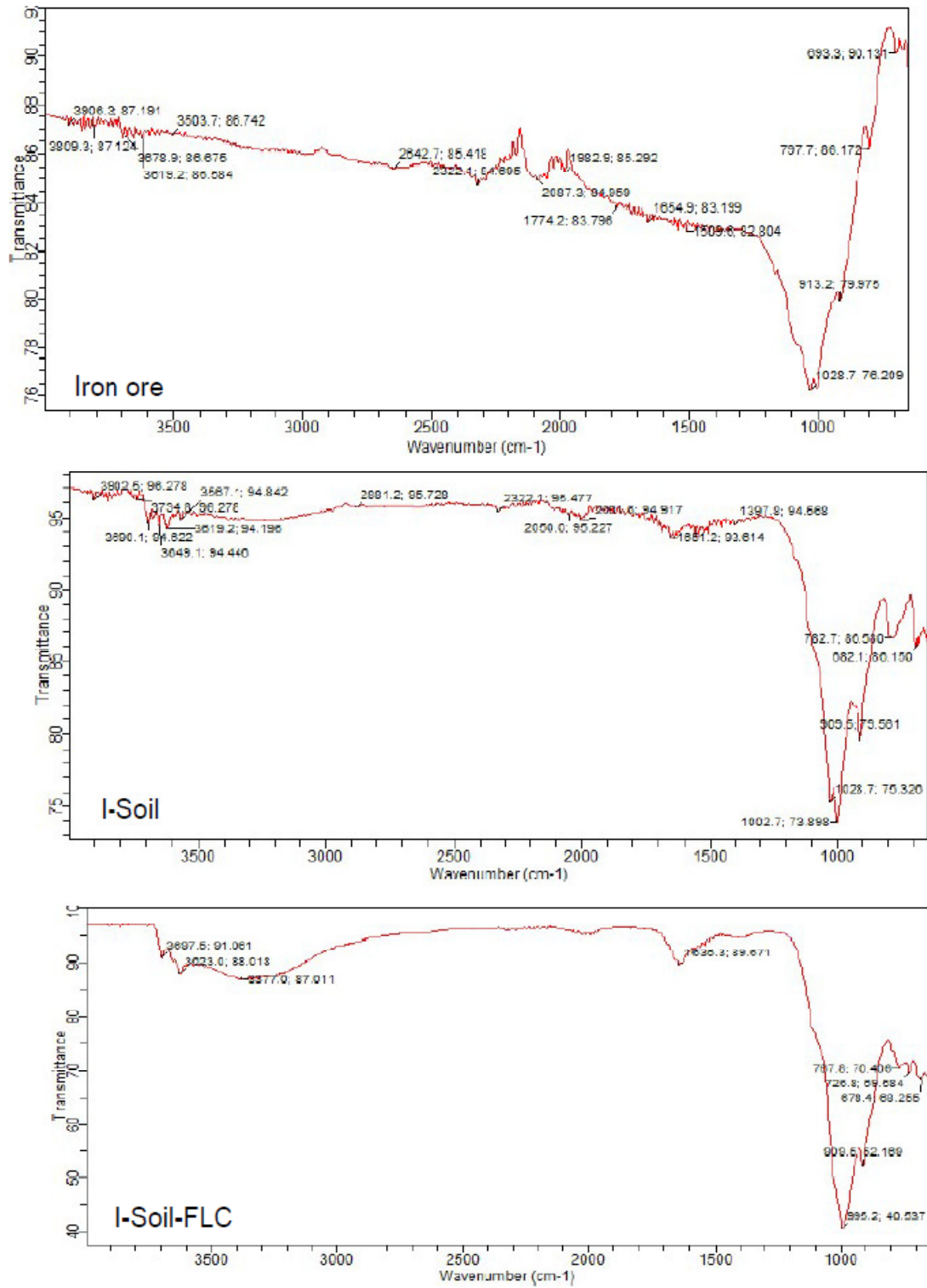


Fig. 4. FTIR spectra of iron ore, ore vicinity soil (I-Soil) and neighboring farmlands soil (I-Soil=FLC)

Table 4. FT-IR analysis of iron ore and soil samples within the ore rich region

Vib. Freq. (cm ⁻¹)	Functional group	Observed vibrational frequencies (cm ⁻¹) for samples				Assignment
		Iron Ore	I-Soil	I-Soil-FLA	I-Ref-Soil	
2322-2005	HPO ₄ ⁻	2332	2001	2005	-	NaHPOH ₂ O
2087-1880	CN ⁻	2087	2001	1830	1880	K ₃ Fe(CN) ₆
1982-1029	Si-O stretching	1029	1029	-	1982	SiO ₂
913-910	Silicate ions	913	910	910	910	SiO ₂
893-882	CO ₃ ⁻	893	882	887	889	K ₂ CO ₃
798-753	Si-O quartz	798	789	790	753	SiO ₂

3.5 UV-Visible of Iron Ore and Soil Samples

Table 5 is the results of wavelengths at maximum absorbance for samples. From the analysis, iron ore and their corresponding soil samples gave the λ_{max} of 334 nm, 331 nm and 324 with the following absorbance 4.770, 2.292 and 1.154 for iron ore, I-Soil and I-Soil-FLA respectively. This close values could be an indication that there is leaching from the parent ore to the environment.

Table 5. UV-Visible for Iron Ore and its corresponding soil

Samples	λ Max. (nm)	Abs.
Iron ore	334	4.770
I- Soil	331	2.292
I-Soil-FLA	324	1.154

3.6 Heavy Metal Analysis

Table 6 shows the mean concentration (mg.kg⁻¹) of heavy metals in iron ore and neighboring soil samples.

3.6.1 Iron concentration

The highest mean concentration of iron was 6898.743 mg.kg⁻¹ for the ore and the lowest was 1793.331 mg.kg⁻¹. This was more than the permissible limits set by the United States environmental protection agency [34] and were higher than that reported in literature [44]. The relatively high Iron could be as a result of the presence of Iron sulphide (marcasite or pyrite) [45].

3.6.2 Lead concentration

The highest mean concentration of lead was 179.59 mg/kg as the lowest was 100.070 mg.kg⁻¹. This was higher than 0.07 mg.kg⁻¹ reported for similar work [44], but lower than the maximum permissible limit of 420 mg.kg⁻¹, set by USEPA. The allowable limits also vary widely with countries 300 mg.kg⁻¹ in United Kingdom and luxem boury 100 mg.kg⁻¹ in France and Austria. Pb values therefore reflect the presence of mine wastes and tailings resulting from mining activities [45].

3.6.3 Copper concentration

Copper mean concentration was 2.822 mg.kg⁻¹ and the lowest was 0.214 mg.kg⁻¹. This was higher than the presented 0.13 mg.kg⁻¹ report [44], but was below the 45 mg/kg set by USEPA. This level poses no threat to the local environment [46]. Although copper Toxicity in human is rare, aquatic organism are more prone at risk from Cu.

3.6.4 Zinc concentration

Zn ranges from 18.308 mg.kg⁻¹ to 7.039 mg.kg⁻¹ in this work. This value was higher than 0.04 mg.kg⁻¹ in literature [44], but lower than 95 mg/kg set for Zc. Zinc is an essential macronutrient for plants but it's phytotoxic in excess phototoxicity may cause decrease crop yield and quality and likelihood and Zn transfer into the food chain.

3.6.5 Nickel concentration

Ni has the average value of 1.348 mg.kg⁻¹ and 0.890 mg.kg⁻¹. The value was higher than 0.15 mg.kg⁻¹ earlier documented [44], but lower than 75 mg.kg⁻¹ maximum permissible limits for

Nickel [34]. Ni is also relatively immobile, limited by co-precipitation with limonite and by hydrolysis.

3.6.6 Cadmium concentration

Cd in the study area has a mean value of 0.060 mg.kg⁻¹ and 0.001 mg/kg. This was lower than 0.18 mg.kg⁻¹ in early findings [47] and lower than the permissible limits by USEPA. Cd is more volatile than most heavy metals and significant amount is released to the atmosphere during the processing also through weathering of the sulphides (abandoned mine wastes). The source of Cd is anthropogenic [45].

3.6.7 Manganese concentration

The highest mean concentration of manganese was 70.560 mg.kg⁻¹ and the lowest was 34.549 mg.kg⁻¹. This was lower than the set legislative values of 770 and 850 mg.kg⁻¹ respectively. The value falls within the acceptable limits. The presence of Mn could be as a result of manganiferous siderite gangue in the area [45].

3.6.8 Chromium concentration

The average concentration of Chromium ranges from 3.771 mg.kg⁻¹ to 0.883 mg.kg⁻¹. Chromium range in this study is lower than 40-90 mg.kg⁻¹ maximum set permissible limit [45]. It was also observed that the level of chromium in this study was far lower than maximum permissible limits of most countries, except for Nether lands and Ontario whose maximum permissible levels are 30 mg.kg⁻¹ and 26 mg.kg⁻¹ respectively. The low values of Cr recorded in the soils around the mines could also suggest very low mobility for these elements during weathering and soil formation.

3.7 Heavy Metal Pollution Assessment for Iron Ore and Neighbouring Soils

Table 7 is a data that summarises the contamination factor in Iron rich soil region based on geo-accumulation index. Results shows that Cd was low in iron ore, I-Soil and I-Soil-FLA, Cr was low in iron ore and I-Soil but moderate in I-Soil-FLA, Ni was discovered to be low in iron ore, I-Soil-FLA but moderate in I-Soil. Mn was low in iron ore, I-Soil-FLA but moderate in I-Soil, Zn

was moderate in I-Soil and iron ore but low in I-Soil-FLA, Cu was found to be low in iron ore and I-Soil but moderate in I-Soil-FLA. Pb was found to be low in iron ore, I-Soil-FLA but moderate in I-Soil while Fe was found to be moderate in iron ore, I-Soil-FLA but considerable in I-Soil.

Computation based on geo-accumulation index classified the soil in relative to the Fe level as “extremely contaminated. Sequel to the loading of soil by other metals, the farmland soils are grouped into strongly contaminated with Pb; moderately contaminated with Mn and Zn and uncontaminated with Cd and Cu [31].

3.8 Comparative Study

Fig. 5 shows some of the trends observed by selected metals. Presents of these metals are responsible for the observed conductivity profile. One way analysis of variance ANOVA was carried out to determine if there is any significant difference in the heavy metals and physicochemical parameters for the mineral rich soils with reference to the control sample. Results shows that there is no significant difference in Cr, Ni and Pb when compared statistically, hence, an indication that the metals are evenly distributed, while that of Cd, Cu, Mn and Zn are significantly different. The physicochemical parameters analysis of variance shows there is significant difference in the pH, conductivity, bulk density, moisture content and particle size.

Generally, it is noteworthy that Mine tailings are among the largest mining wastes on Earth and can reach surface areas of up to 52 km² [48]. Soil metallic load arising from mine tailing is as critical as those exposed by weathering of mineral ores. Tailings disposal options entails finding the best location (not agricultural soil) for mine tailing from technical, environmental and economical standpoints [49]. Findings in this study generally agrees with a report on two rural communities located in the vicinity of mining sites where the pollution load of the areas are probably linked to increasing mine activities and the lack of appropriate measures to counteract its effects, causing a progressive pollution of soil with heavy metal emissions in the studied region [50].

Table 6. Mean concentration (mg.kg⁻¹) of heavy metals in soil around iron ore contaminated farmlands

Toxic metals	Soil samples					
	I-Soil-FLA	I-Soil-FLB	I-Soil-FLC	I-Soil	I- Ref-Soil	Iron Ore
Cd	0.045 ± 0.0003	0.022 ± 0.0005	0.019 ± 0.0004	0.002 ± 0.0002	0.060 ± 0.0004	0.001 ± 0.0003
Cr	2.930 ± 0.0007	2.184 ± 0.0003	2.217 ± 0.0005	1.928 ± 0.0007	3.771 ± 0.0003	0.883 ± 0.0057
Ni	1.319 ± 0.0018	0.888 ± 0.0034	1.065 ± 0.0037	1.348 ± 0.0038	0.890 ± 0.0034	0.833 ± 0.0020
Mn	51.28 ± 0.0008	34.55 ± 0.0009	41.61 ± 0.0005	70.56 ± 0.0009	48.56 ± 0.0013	41.81 ± 0.0007
Zn	15.47 ± 0.0007	8.710 ± 0.0012	11.68 ± 0.0015	18.02 ± 0.0012	7.039 ± 0.0045	18.31 ± 0.0009
Cu	2.822 ± 0.0013	1.287 ± 0.0007	2.193 ± 0.0012	0.968 ± 0.0004	2.361 ± 0.0006	0.214 ± 0.0003
Pb	109.9 ± 0.0001	100.9 ± 0.0005	100.1 ± 0.0002	176.6 ± 0.0026	150.1 ± 0.0003	103.1 ± 0.0003
Fe	2476.133±0.002	3082.884±0.001	1793.331±0.001	6898.743±0.001	2220.918±0.001	6291.989±0.003

Table 7. Geo-accumulation index of heavy metals in soils from farmlands near iron ore deposits (Based on legislative reference as Bn values)

Toxic metal	Geo-accumulation index (Igeo) values				Igeo grouping	Soil quality w.r.t. metal level
	I-Soil-FLA	I-Soil-FLB	I-Soil-FLC	I-Soil		
Cd	-1.875	-0.533	-0.596	-1.574	< 0	Uncontaminated
Cr	1.469	1.862	1.869	1.808	1-2	Moderately contaminated
Ni	0.046	0.073	0.152	0.254	0-1	Uncontaminated to moderately contaminated
Mn	2.746	2.663	2.744	2.973	2-3	Moderately to strongly contaminated
Zn	0.609	0.287	0.414	0.603	0-1	Uncontaminated to moderately contaminated
Cu	-0.846	-0.066	0.165*	-0.19	< 0	Uncontaminated
Pb	3.138	3.129	3.125	3.372	3-4	Strongly contaminated
Fe	4.146**	3.836	3.6	4.186**	4-5	** extremely strongly contaminated

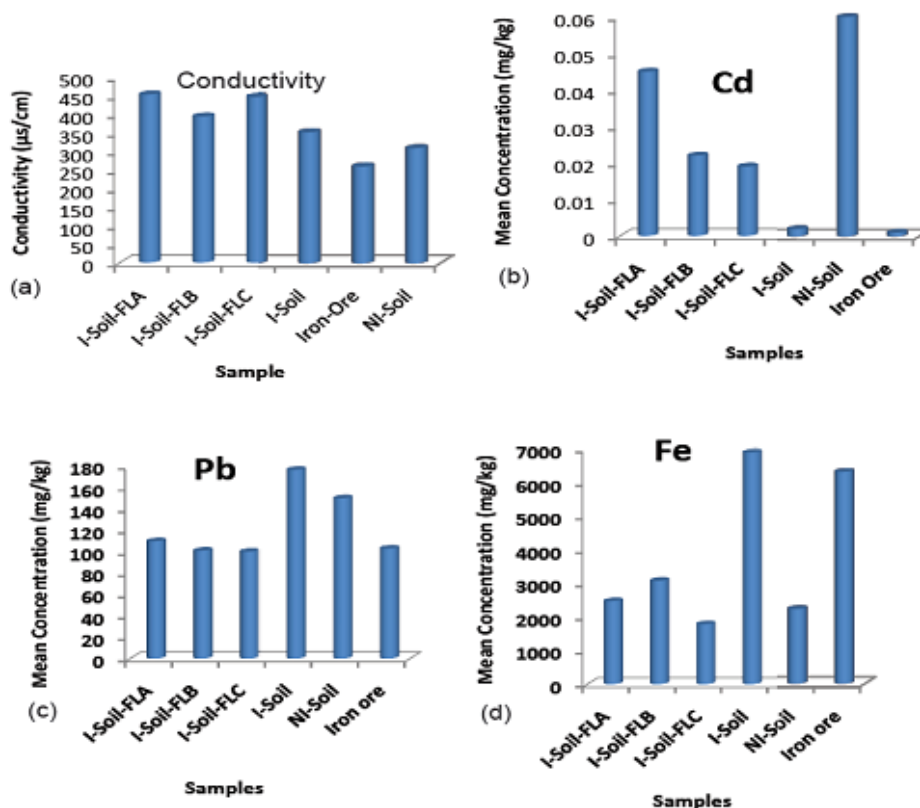


Fig. 5. Charts, showing (a) conductivity values and level of (b) cadmium (c) lead and (d) iron in farmland soils near iron ore depot

4. CONCLUSION

Our results from FTIR, SEM and UV-Vis, indicated that mineral ore and soil physicochemical parameters as well as characteristics are in good agreement in terms of quality and compositions. Analysis of Iron rich soil indicates that the pH of Iron Ore falls within the neutral boundary. The conductivity measurement was found to be high as a result of soluble salt in the soil. Analysis for bulk density was found to be low and may be as a result of increase soil organic matter. Moisture content analysis was also on the high side. The analyzed particle size indicates high level of sand followed by clay and then silt. The pattern below indicates the trend of heavy metal concentration in Iron rich soil. For Iron ore; Fe > Pd > Mn > Zn > Cr > Ni > Cu > Cd . I-Soil and the farmland soils I-Soil-FLA, B and C gave similar metal load trend as the mineral ore. This is an indication of mine tailing and metal distribution from ore to farmland soils. The computed contamination factor of the soil pollution by heavy metals shows that, in Iron

rich soil, Cd, Cr, Ni, Mn, Cu and Pb were low; Fe and Zn were moderate while I-Soil Fe was considerably high. Computation based on geo-accumulation index classified the soil in relative to the Fe level as “extremely contaminated. Based on the highlights from this study, valuable information about the status of heavy metal level is presented as baseline data for awareness on possible metal leaching, mobility and distribution along the mine region. It is strongly recommended that there is a need to develop an environmental monitoring and management programme on heavy metals.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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