

Comparative Assessment of Soil and Selected Crop in Cement Dust Contaminated Environment in Okpella Area of Edo North, Nigeria

Abstract

The research was designed to compare the degree of contamination of soil and selected crops by cement dust generated during cement industry activities. Two types of soils were investigated. Soil obtained near the cement industry (OS1) and the soil obtained in a location far from the site of the cement industry (AS2). Only cassava was studied but collected at two different locations. Crop sample collected near the cement industry (OC1) and the one collected at a site far from the cement industry (AC2). The physicochemical properties of the soil samples were determined by analyzing for their percentage nitrogen (N), organic matter (OM), phosphorous (P), potassium (K), electrical conductivity (EC), moisture content (MC), bulk density (BD) and hydrogen ion potential (pH). The proximate composition of the crop samples was determined by analyzing for moisture content, crude protein, ash content, ether extract, crude fibre, dry matter, and carbohydrate. The method used was in accordance with the Association of Official Analytical Chemists'. The samples were characterized for the presence of functional groups using Fourier Transform Infrared (FT-IR) spectroscopy. X-ray Diffractometer (XRD) was used to determine the mineral composition and the heavy metals were determined using the Atomic Absorption Spectroscopy (AAS) method of analysis. The result showed that the percentage of P (28.6 ± 0.01) and K in AS2 was higher than in OS1 (21.6 ± 0.07). The OM in AS2 (2.34 ± 0.01) was higher than in OS1 (2.17 ± 0.01). The values obtained for EC were OS1 (145.7 ± 0.01) and AS2 (115.4 ± 0.28). The concentration of the selected elements did not exceed the maximum allowable amount. Fe has the highest concentration in soil and crop samples. The obtained value for ash content in OC1 was 4.62 ± 0.00 and AC2 was 2.39 ± 0.01 . Carbohydrate has 74.4 ± 0.01 in OC1 and 83.4 ± 0.05 in AC2, however moisture content in OC1 was 7.17 ± 0.03 and 6.86 ± 0.03 in AC2. The results also showed the presence of various functional groups and revealed the types of minerals in the samples.

Keywords: Environment, soil, cassava, cement dust, heavy metals

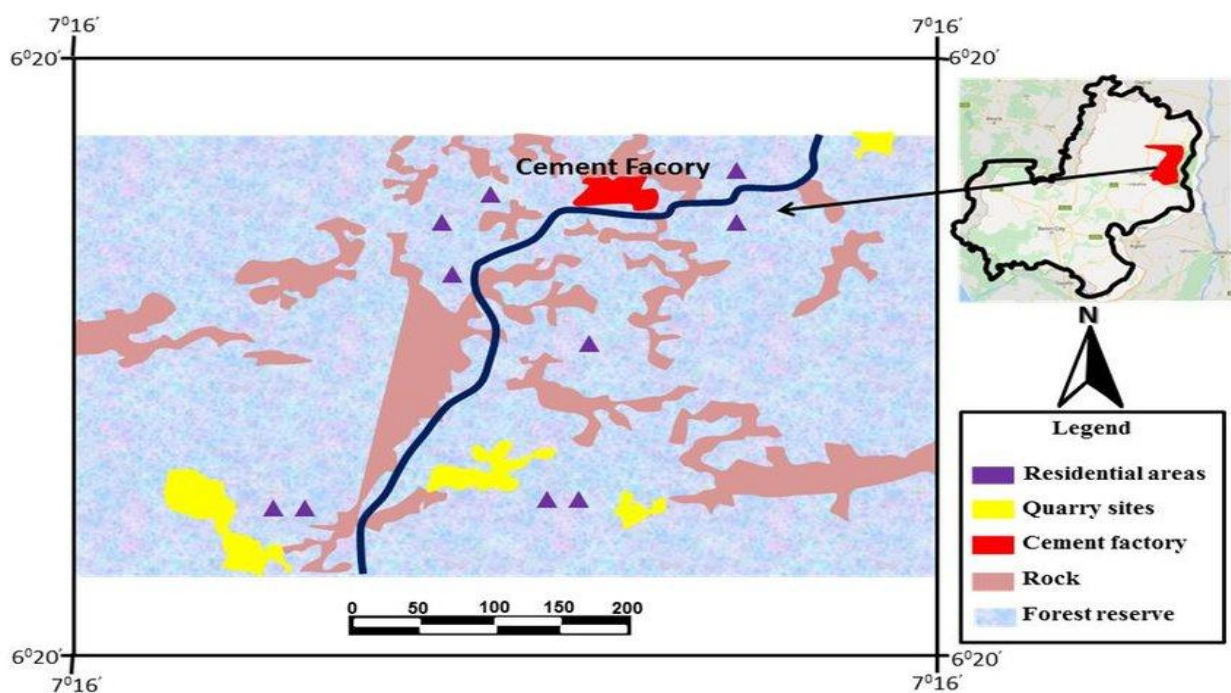
Introduction

Industrial environments are associated with the emission of toxic elements, particularly heavy metals, as a result of industrial activities and attendant environmental pollution, which in turn contributes significantly to human health challenges. It is known that the industries emit dust particles of various sizes, volatile substances and hazardous metals during cement production. The cement industries contribute to the environmental imbalances by altering the composition of the environment, resulting in pollution. Since the advent of human search for innovation, the development activities of industries and their effluents have been a primary concern in the environment and the activities of cement over the years have threatened the survival of our ecosystem. Plants and animals in the industrial areas, water, air and land are polluted by these obnoxious substances released into the environment by the cement plants. Ramesh, Ahmed, and Koperuncholan, 2014 have reported that pollutants and other toxic effluents released from the cement and mining industries and processes of raw materials including limestone, dolomite are sources of environmental pollution and toxic substances. The contamination of the major environmental components, including air, land, and water, has resulted from the presence of these toxic substances. Malthotra (2002) estimated that the cement manufacturing industries in Poland contributes to about 7 % of the overall greenhouse gases emissions that are released into the earth's atmosphere. High concentration of greenhouse gases has led to global warming. This warming has led to various adverse consequences, including the melting of polar ice, more frequent instances of flooding and drought, and alterations to the natural habitats of plants and animals (OlatunbosunSawa, Jibrin, Ilori, 2020). In addition, gaseous substances including carbon oxides (CO and CO₂), nitrogen oxides (NO_x), sulphur dioxide (SO₂), and dust are discharged into the atmosphere by the cement manufacturing industries as reported by Kampa and Castanas, 2008, Pregger and Friedrich, 2009. In the twenty-first century, the release of potentially dangerous metals and resulting risk of food safety have become major environmental concerns (Hailu Reta and Leta Damo (2020). Elements classified as heavy metals have specific densities more than 5 g/cm³. Metals with this property have the potential to cause harm or destroy properties, living organisms and the ecosystem at large (Järup, 2003). As a consequence of their non-biodegradable nature, heavy metals readily accumulate in soil that has been contaminated, posing a risk to human health through the ingestion of contaminated crops and vegetables.

The study

The study location is the immediate environment of the BUA cement plant situated in Okpella.

Okpella is a town situated along the Federal highway that connects Abuja and Benin. Based on the latest census figures, the town has a population of 20,562 and one of the three major towns that constitute Etsako Local Government Area in Edo State. Okpella is known for its natural mineral resources based on sedimentary rocks including marble, calcium granite, feldspar, soap stone, clay, and limestone. The indigenous people are predominantly farmers. They engage in substantial production or cultivation of yams, cassava, tomatoes and ogbono. Okpella lies between $7^{\circ} 16'$ to 12° N latitude and $6^{\circ} 20'$ to 46° E longitude



Pic 1. Study location

Materials and Methods

Samples Collection

Soil sample was collected from the industrial study area at a depth of 0 to 15 cm using a stainless steel spade. Crop sample (cassava tubers) was collected at the same. Soil and crop (cassava) samples were collected using the same method at non-industrial study area. The samples were collected into polyethylene bags labeled and properly tied. All the samples were collected during rainy season. Analytical grade chemicals and reagents were used in this study.

Preparation of Sample

Soil samples were air-dried for three days in the laboratory at ambient temperature and then dried for 2 hours at 105 °C in an oven. The dried samples were ground to pass through 100 µm mesh sieve and stored in a close air-tight container for further analysis. The soil sample collected from the industrial site at Okpella was labelled OS1 while the soil sample collected from non-industrial site at Auchi was labelled AS2, which correspond to the control.

The crop samples were also air-dried for seven days and then oven-dried at 105 °C for 2 hours. The dried samples were ground to pass through 100 µm mesh sieve and stored in a close air-tight container for further analysis. Moreover, the cassava powder prepared from cassava tuber collected from industrial site at Okpella was labelled OC1 while cassava collected from non-industrial site at Auchi was labelled AC2.

Characterization of Samples

The samples were characterized using the following instruments; (1) FT-IR (Infrared Spectrometer Varian 660 MidIR Dual MCT/DTGS Bundle with ATR), (2) X-ray Diffractometer (XRD) and Atomic Absorption Spectroscopy (AAS). The XRD was used to determine the mineral compositions, while the FTIR Spectroscopy was used to investigate the presence of functional groups in the samples. AAS was used to determine the concentration of the heavy metals in the samples. The proximate compositions of the samples were determined according to the methodologies outlined in the AOAC 2009 report.

Results and Discussion

Table 1 shows that the physio-chemical properties of soil such as organic matter, electrical conductivity, soil pH and moisture content influence the concentration of potentially toxic metals in the soil in a large quantities as well as on the bio availability and bio accumulation in plant. The soil organic matter obtained from this study showed that the value is between 2.17 ± 0.01 and 2.340 ± 0.01 in the OS1 and AS2 respectively. The value (2.17 ± 0.01) obtained in OS1 could be due to the decay of microorganisms as a result of industrial activities. Low level of organic matter can increase soil erosion processes while high level of organic matter could affect the pH by lowering its level (Kekane *et al.*, 2015).

The pH values of the soil samples is between 6.60 ± 0.06 and 6.83 ± 0.03 . AS2 sample has the highest pH value (6.83 ± 0.03). The soil samples showed the availability of nutrients such as nitrogen (N), phosphorus (P), potassium (K). The N, P, and

K values obtained with respect to AS2 range from 0.29 ± 0.00 to 28.6 ± 0.01 while the values with respect to OS1 range from 0.55 ± 0.01 to 23.6 ± 0.01 . The results show that nutrients availability was higher in AS2 than OS1 except for nitrogen (N) which was higher in OS1. The study showed that OS1 and AS2 pH values were within the standard range (6.5 to 8.5) set by the World Health Organization (WHO). The electrical conductivity (EC) of the soil samples is between 115.4 ± 0.28 and $145.7 \pm 0.01 \mu\text{S}/\text{cm}$. Soil EC is an important indicator of soil salinity and a measure of the amount of salt in the soil but does not indicate the specific salt or ions that might be present. It is an indicator of salts such as sodium (Na), potassium (K), chloride (Cl), Sulphate (S), (Ullman, 2013). The result showed that the EC of OS1 and AS2 is low because EC of soils is less than $200 \mu\text{S}/\text{cm}$ does not contain sufficient nutrients for plants and could have a disinfected soil with low microbial activity, (Verma *et al.*, 2015).

A total of nine heavy metals were analyzed in the soil and crop samples for this research. The heavy metal concentration in OS1 was between 0.001 ± 0.00 to 228.6 ± 0.03 . The lowest concentration was found for mercury (Hg 0.001 ± 0.00) while the highest concentration was found for iron (Fe 228.6 ± 0.03). In AS2 which correspond to the control sample, the concentration of heavy metals range from 0.001 ± 0.00 to 252.03 ± 0.15 . Mercury (Hg, 0.001 ± 0.00) has the lowest concentration while iron (Fe, 252.03 ± 0.15) has the highest concentration. It shows that the concentration of Iron (Fe) was the highest in OS1 and AS2. The lowest concentrations were recorded for Mercury (Hg) in OS1 and AS2.

Table 1: The physicochemical properties of OS1 and AS2.

Parameter	OS1	AS2
N (%)	0.55 ± 0.01	0.29 ± 0.00
OM (%)	2.17 ± 0.01	2.34 ± 0.01
P (%)	23.6 ± 0.01	28.6 ± 0.01
K (%)	18.4 ± 0.14	21.6 ± 0.07
EC (%)	145.7 ± 0.01	115.4 ± 0.28
MC (%)	6.62 ± 0.01	6.56 ± 0.04
BD	1.09 ± 0.00	1.10 ± 0.03
Ph	6.60 ± 0.06	6.83 ± 0.03

The obtained values are averages \pm standard deviation of duplicated determination

The accumulation of heavy metals in the soil was presented in Table 2. The concentration order for OS1 was as follows; $\text{Hg} < \text{Co} < \text{Cu} < \text{Pb} < \text{Mn} < \text{Cr} < \text{Zn} < \text{Fe}$ while AS2 was in the order $\text{Hg} < \text{Co} < \text{Ni} < \text{Pb} < \text{Cu} < \text{Mn} < \text{Cr} < \text{Zn} < \text{Fe}$. The findings indicate that iron (Fe) has the highest

concentration in OS1 and AS2 (228.6 ± 0.03 and 252.0 ± 0.15 respectively while OC1 and AC2 (2.32 ± 0.01 and 1.97 ± 0.00). The results showed that Co and Hg were below detection limit. It is observed that the pollution is not severe as all the selected elements do not exceed the maximum amount allowed. Based on World Health Organization (WHO) /Food and Agriculture Organization (FAO) guidelines. Although the highest obtained value for iron (Fe) could be due to its occurrence presence in the earth's crust, this justifies its use as reference metal in the computation of enrichment factor (Ala *et al.*, 2013).

Table 2. Heavy Metals concentration

Metals	concentrations (ppm)			
	OS1	AS2	OC1	AC2
Mn	0.370	0.490	0.190	0.210
Cu	0.310	0.270	0.120	0.170
Cr	0.820	0.820	0.070	0.100
Co	0.010	0.000	0.000	0.000
Hg	0.000	0.000	0.000	0.000
Ni	0.040	0.060	0.000	0.010
Fe	228.600	252.000	2.320	1.970
Pb	0.320	0.270	0.000	0.010
Zn	0.960	1.450	0.610	0.400
mean value	25.714	28.373	0.368	0.319

The obtained values are averages \pm standard deviation of duplicated determination

The result of the proximate composition analysis of OC1 and AC2 are presented in the table 3. A greater concentration of moisture was detected in OC1. The values showed that moisture content of the sample was moderate, suggesting that it can be conveniently stored for a long period of time as this will prevent the growth of microorganisms and thus extends the shelf-life of both OC1 and AC2. The values obtained are acceptable for the established aim, achieve a stable shelf-life (< 20 % moisture) and agree with the values previously reported by Kayisuet *al.*, 1981, Gwenfogbeet *al.*, 1988, Daramola and Osanyinlusi, 2006.

Ash refers to the concentration of minerals or inorganic residue that remains after either ignition or complete oxidation of organic matter in a food stuff. It is used for nutritional assessment. The percentage ash content in OC1 and AC2 is between 2.39 ± 0.01 and 4.62 ± 0.00 . The low value found in OC1 could be due to evaporation of some of volatile minerals due to heat.

Carbohydrates are important in food as a major source of energy, to influencing crucial textural properties and dietary fiber which affects physiologically processes.

The result of carbohydrates obtained from the samples by difference showed that AC2 was

higher (83.4±0.05) while OC1 was (74.4±0.01)

Fats refer to those lipids that are solid at room temperature. Analysis of fats in food is important for accurate nutritional labelling, to determine whether the food meets the standard of identity and to ensure that the product meets manufacturer's specifications. Fat values obtained for OC1, AC2 were (4.54±0.07) and (2.36±0.00) respectively. Fiber is essentially the sum of the indigestible components of food or food product. The fiber content of both samples range was (1.61±0.00) and (2.16±0.35). Protein are abundant components of all cells and are important for biological functions and cell structure except the storage proteins. The range of crude protein percentage is 3.37±0.02 in AC2 and 7.15±0.01 in OC1

Table 3. Proximate Analysis of OC1 and AC2

Parameters	OC1	AC2
Moisture Content	7.17±0.03	6.86±0.03
Ash Content	4.62±0.00	2.39±0.01
Fat	4.54±0.07	2.36±0.00
Fiber	2.16±0.35	1.61±0.00
protein	7.15±0.01	3.37±0.02
CHO	74.4±0.01	83.4±0.05

The obtained values are averages ± standard deviation of duplicated determination

Figure 1 is the FTIR spectrum of OC1. The peak appearing at 3926.4 cm⁻¹ is due to O-H stretching vibration of hydroxyl group. The peak at 3312.65 cm⁻¹ corresponds to the stretching vibration of OH while the absorption peak at 2927.50 cm⁻¹ is due to the stretching vibration of CH₂ of the alkyl group of the ammonium salt present in the sample. The peak at 2850.31 cm⁻¹ is as a result of the presence of OH stretching vibration hydroxyl group due to the water molecule adsorbed in the sample. The absorption peak at 2312.88 cm⁻¹ is due to the CO₃²⁻ (calcite) stretching of carbonates compounds while the peak at 1650.03 cm⁻¹ indicates the presence of asymmetric OH stretching hydroxyl group of water molecule. The absorption peak at 1510.61 cm⁻¹ shows the presence of asymmetric Si-O silicate stretching vibration while the peak at 1450.77 cm⁻¹ is due to Si-O-Si stretching silicates. However the absorption peak at 1250.57 cm⁻¹ indicates the presence Al-OH vibration due to aluminum deformation. The peak at 1050.55 cm⁻¹ is due to the stretching vibration of Si-O (silicates plane). The absorption peak at 850.44 cm⁻¹ shows the presence of O-H deformation due to hydroxyl/aluminum while the peak at 618.33 cm⁻¹ is due to the Al-O (silicates aluminum Si group).

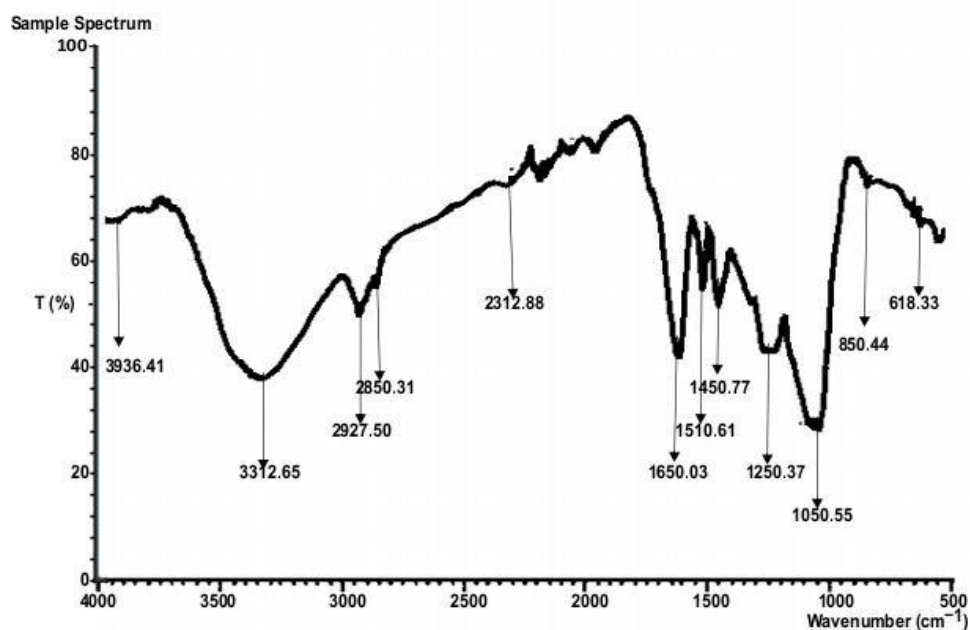


Figure1:FTIRSpectrumofOC1

Figure2showstheFTIRspectrumofAC2.Theabsorptionpeakat3775.10 cm^{-1} is due to the presence of the OH stretching vibration of the hydroxyl group. Thepeakappearingat3350.19 cm^{-1} indicates the Si-OHstretchingvibration of silanolgroupwhile the absorption peak at 2775.84 cm^{-1} is due to the stretching vibration of CH_2 (alkanes). The appearance of a peak at 1250.78 cm^{-1} indicates H-O-Hbending vibration (hydroxyl group). The absorption peak at 1150.13 cm^{-1} is due to the stretching of silicate vibration (Si-O)whilethepeakat1051.42 cm^{-1} isduetoSi-O- Si stretching vibrations (silicates compounds). The peak that appears in thespectrum at 974.82 cm^{-1} corresponds to Al-OH-Al (aluminates). The absorptionpeakat800.64 cm^{-1} indicates thepresenceofSi-OandSi-O-Al(silicates/aluminates). However the absorption band at 550.30 cm^{-1} is due to the stretching vibration of Si-O-Al (silicates/aluminates).

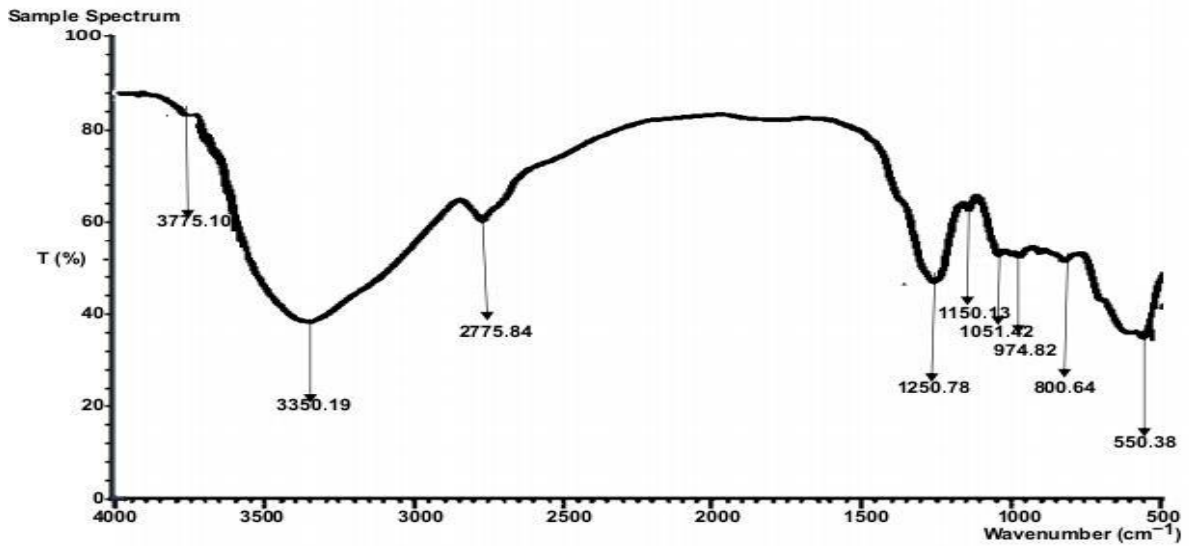


Figure2:FTIR Spectrum of AC2

Figure 3 is the FTIR spectrum of OS1. The peak appearing at 3750.12 cm^{-1} indicates the presence of O-H stretching vibration of hydroxyl group, while the peak at 3350.19 cm^{-1} corresponds to OH stretching vibration of hydroxyl group. A peak at 1960.33 cm^{-1} corresponds to the stretching vibration of CH_2 (alkanes). The absorption band at 1600.85 cm^{-1} is the region corresponding to the stretching vibration of OH due to the presence of adsorbed water in the sample (hydroxyl group). The peak at 1300.28 cm^{-1} is due to the oscillation of the CO_3^{2-} stretching carbonates (calcite). The absorption band 1150.03 cm^{-1} shows the presence of sym bonds while the peak at 1000.36 cm^{-1} corresponds to the asymmetric stretching vibration of the Si-O silicate. The absorption peak at 892.57 cm^{-1} is due to the vibration of the Si-O-Si stretching silicates and at 750.14 cm^{-1} , the peak corresponds to Al-OH deformation of the aluminum compounds. The peak appearing at 618.33 cm^{-1} indicates the presence of OH bending vibration of the hydroxyl group. The absorption band at 550.28 cm^{-1} is due to the presence of O-Si-O/O-Al-O bending and silicates/ aluminates stretching vibration.

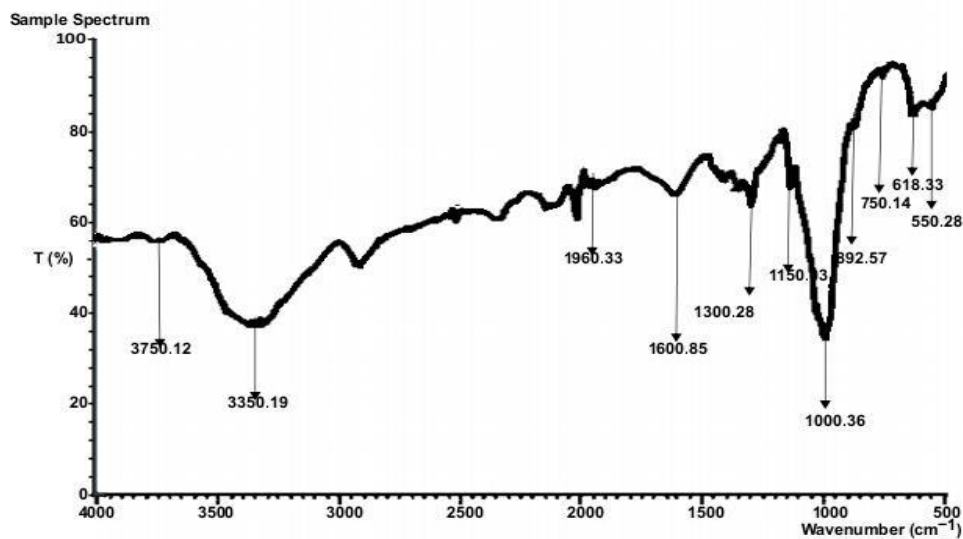


Figure 3: FTIR Spectrum of OS1

Figure 4 is the spectrum of AS2. The absorption peaks at 3312.65 , 2927.50 and 2850.31 cm^{-1} correspond to the stretching of OH, OH vibration elongation due to hydroxyl group in the dioctahedral part of the mineral, OH stretching vibration (hydroxyl group) due to the adsorbed water presence in the samples respectively. The peak at 1711.85 cm^{-1} is due to the asymmetric stretching vibration of the OH hydroxyl group of water while the peak at 1594.18 cm^{-1} indicates the presence of asymmetric stretching vibration of Si-O silicates. The absorption peak at 1500.29 cm^{-1} indicates the presence of calcite- CO_3^{2-} stretching carbonate vibration in the soil sample. The peak at 1442.63 cm^{-1} is attributed to the vibration of Si-O-Si stretching silicates while the absorption peak at 1206.16 cm^{-1} corresponds to the vibration of Al-OH aluminum compounds. However, the peak at 1050.55 cm^{-1} shows the presence of stretching vibration of Si-O (silicates) and the absorption band appearing at 800.03 cm^{-1} is due to the presence of OH deformation mode of hydroxyl/aluminates (Al-Al-OH or Al-OH-Al)

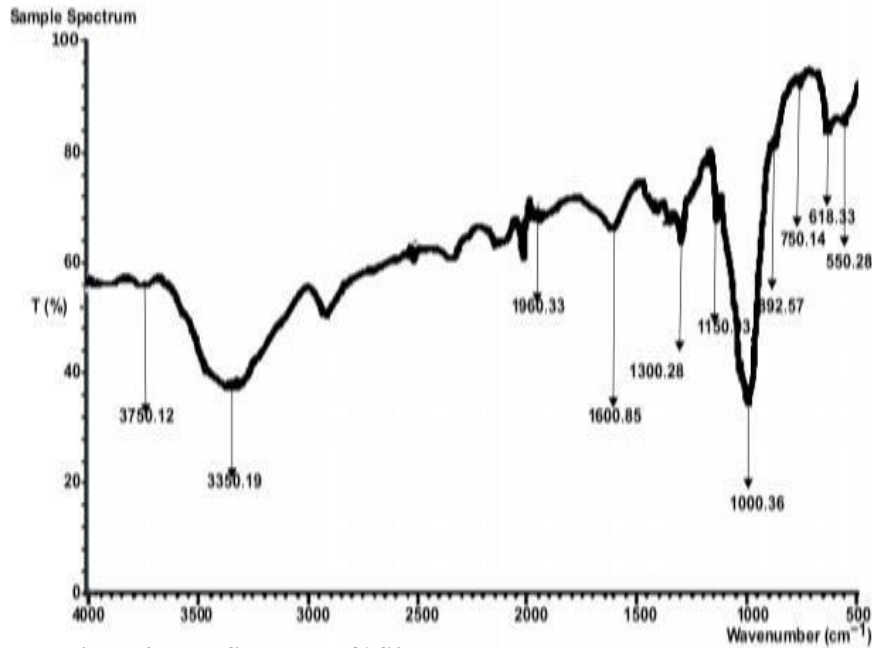


Figure4:FTIR Spectrum of AS2

XRDSpectrums

X-ray diffraction (XRD) was used to analyze for the mineralogical composition of the samples and the representative XRD patterns are shown below. The XRD indicates crystalline orthorhombic phases. The background and peak positions were identified and based on the peak positions and intensities. Figure 5 is the diffractogram pattern of the OS1. The composition of the intensities in percentage and the corresponding minerals at 20 degrees are listed below. 14.00(3.30), 26.50(21.81), 27.62(15.85), 30.41(5.27), 33.00(4.41), 34.00(3.61), 38.97(11.43), 41.00(9.53), 46.00(2.64), 55.62(5.29), 65.00(3.52), 67.00(4.40), and 78.00(4.01) were for Quartz, Quartz, Hematite, Anatase, kaolinite, Quartz, kaolinite, Muscovite, Microcline, Calcite, kaolinite, kaolinite, and kaolinite respectively. The result showed Quartz to be more abundant (21.81 %), followed by kaolinite (16.34%), Hematite (15.85%).

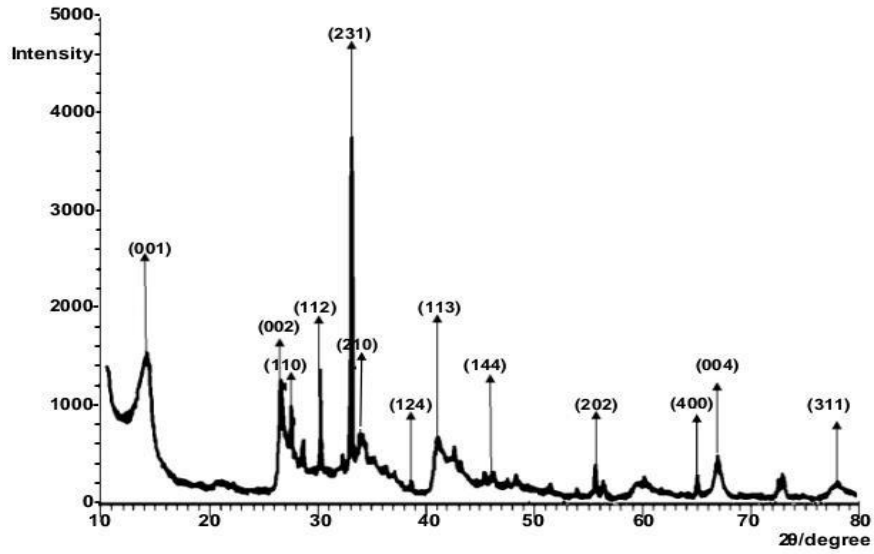


Figure5:XRDSpectrumofOS1

Figure6isthediffractogramofAS2.Theintensitiesat20degreecorresponding to the sample and the corresponding minerals are listed below. Theintensitiesat13.29,22.00,27.64,35.50,37.21,43.00,50.71,60.20,68.79and78.00 wererecordedforkaolinite,Quartz,Quartz,kaolinite,Quartz,Muscovite,Microcline,Cristobalite, Calcite,and Halloysite respectively.

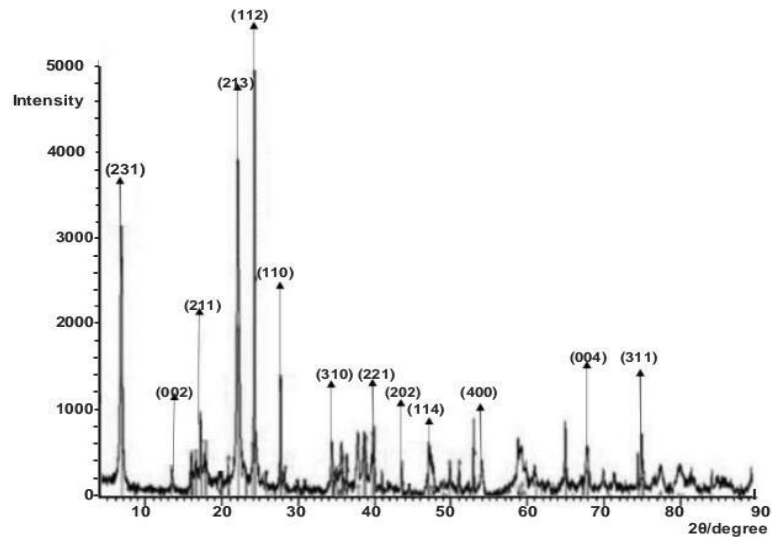


Figure6:XRDSpectrumofAS2

Figure 7 is the diffractogram of AC2. The intensities at 20 degree are asfollowsandthecomposition(%)inparentheses;13.00(3.30),16.50(21.81),28.61(15.85),29.94(5

.27),31.10(4.41),36.23(3.61),37.40(11.43),39.94(9.53),
 44.23(2.64),50.37(5.29),58.00(3.52),62.50(4.40)and76.00(4.01)wererecorded
 forQuartz,Quartz,Hematite,Anatase,Quartz,Quartz,kaolinite,Muscovite,Microcline,Calcite,An
 atase,Quartz,kaoliniterespectively.Theresultindicates that Quartz was much in abundance
 (21.81 %) followed by Hematite, (15.85 %),kaolinite (11.43%).

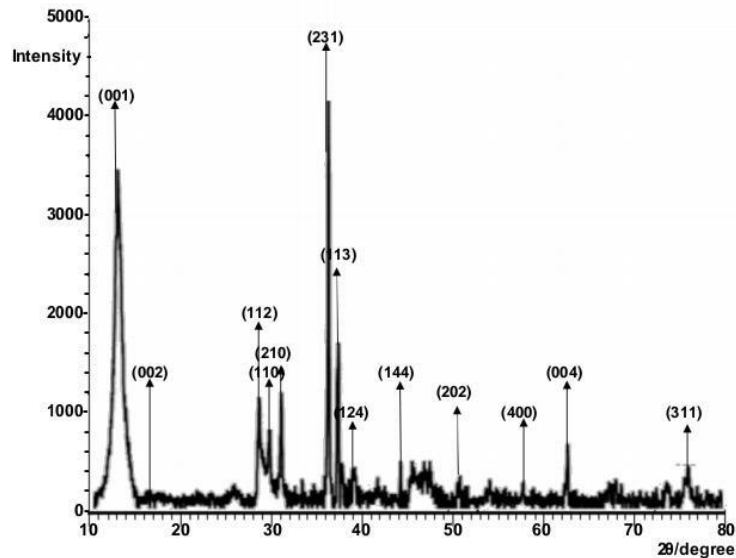


Figure7:XRDSpectrumofAC2

Figure 8 is the diffractogram of OC1. The intensities are recorded at 20 degree. The intensities are listed below with their composition and corresponding minerals. 11.98(3.81), 20.64(10.89), 26.50 (24.64), 34.50 (2.09), 36.43 (20.92), 42.50(5.15), 50.14(17.74), 60.20(4.84), 68.79(3.66), and 78.00(6.29) were kaolinite, Quartz, Quartz, kaolinite, Quartz, Muscovite, Microcline, Cristobalite, and Halloysite respectively. The result shows that the sample was much in Quartz.

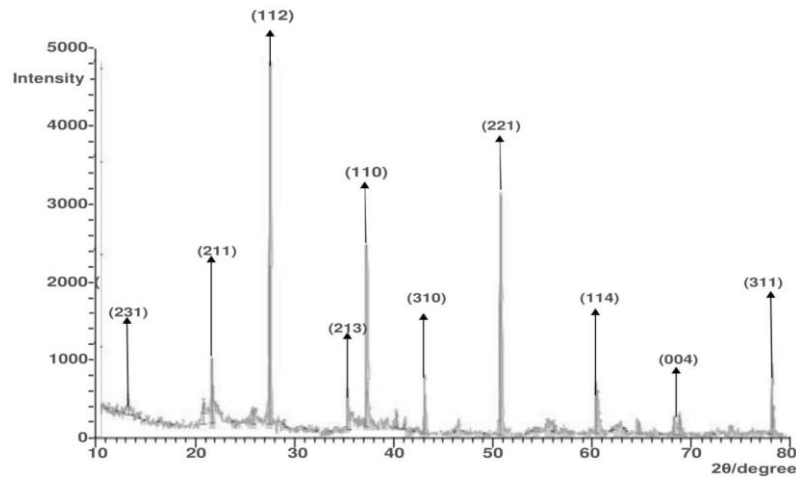


Figure8:XRDSpectrumofOC1

Conclusion

Heavy metals are potential pollutants which are commonly found in manufacturing industries particularly in cement industries. The study investigated the level of heavy metal contamination in the soil and selected crop near a cement industry and another soil and crop samples far from cement industry location. The concentration of the elements did not exceed the maximum allowable amount. The study found that nutrients availability were much in AS2 and the pH was within the standard range in both samples. The moisture content in OC1 and AC2 was moderate indicating that the samples can be stored for a long period of time, with potential to inhibit the growth of microorganisms and thus extending the shelf life. In generally, the outcome of the research could be due to factors such as the season of sampling, climate, and the nature of soil which could be responsible for the concentration of the selected heavy metals and other parameters in the samples (soil and crops). **The XRD revealed the mineral composition of the soil samples and the FTIR showed the presence of various functional groups in the samples.** Further research may be conducted at different times and seasons that vary from the current research conditions and factors.

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