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UV/VIS Characterization and FT-IR Analysis of Harmattan Dust across Sub-Sahara Region of Africa

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Abstract: The suspended dust particles that blow across Nigeria as a result of north-east trade wind emanating from the Sahara desert annually are locally referred to as Harmattan. Suspended dust samples were collected across ten different stations in Nigeria; namely: Maiduguri (11°49'N, 13°09'E), Potiskum (11°43'N, 11°02'E), Bauchi (10°17'N, 09° 48'E), Jos (9°55'N, 8°55'E), Lafia (08°49'N, 07°50'E), Abuja (09°09'N, 07°11'E), Minna (9°36'N, 06°35'E), Ilorin (8°36'N, 4° 35'E), Oyo (8°12'N, 3°42'E) and Iwo (7°63'N, 4°19'E) and analyzed using Fourier Transform Infrared (FT-IR) and UV-Visible spectroscopy. The quantitative, qualitative and optical characterization analyses were carried out on all the samples collected across all the stations considered, in order to obtain the functional groups and some elements present in the samples. The FT-IR spectra peaks show that the transmittance waveband from 3337.8 cm⁻¹ to 3291.2 cm⁻¹ corresponds to the Hydroxyl group, H-bonded OH stretch in plane and out of plane bonds for all the stations considered. These bonds represent the presence of transition metals and unsaturated bonds found in the samples, which include K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Mo, As, Zr, Pb, V, Sr, Cr and Ce. The samples collected across all stations have maximum UV absorbance peaks at around 210 nm waveband and weak visible light absorbance peaks (orange - red spectra) around 620 nm and 700 nm. The study concluded that the transmittance waveband, the waveband absorbance peaks and the elemental composition of the dust samples analyzed vary from station to station. This study will however recommend that further study be made for the purpose of environmental awareness.

Keywords: Harmattan, Particles, FT-IR, UV, Dust.

Introduction

Dust pollution is a common occurrence in the Sub-Sahara region of Africa. This pollution is a common environmental problem in most parts of West Africa, Sunnu *et al.* [1]. It is a natural occurrence to observe that the atmosphere appears polluted with dust particles from various sources, including vehicular exhaust, untarred road, construction sites, bush burning, soil and rock material haulage, open refuse burning and livestock movement, as reported by Sunnu et al [1]. These airborne particles generally affect activities in the country differently, Sunnu *et al*. [1].

Harmattan, which has its original name from Twi language of the Arabic, meaning "haram" (Falaiye and Aweda [2]). This started from the month of November to March of every year. However, during this period of Harmattan, the prevailing wind affects both the domestic and commercial activities across the country (Falaiye and Aweda [2]).

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This dust reduces visibility and contains different elements, which suggests different sources of the particles, Sunnu *et al.* [1]. Many researchers have established that the major source of the dust includes the Bodele Depression (Lake Chad) with the largest reservoirs of dust (Anon [3], Engelstaedter *et al.* [4], Brooks and Legrand [5], Washington *et al.* [6] and Prospero *et al.* [7]). This northeast trade wind blows over the Sahara dust and moves along the trajectory of Nigeria towards the Gulf of Guinea and beyond. The Sahara dust storms as reported by BBC [35] located in the Chad basin, see Fig. 1.



FIG. 1. Sahara dust storm. Source: BBC [35].

The height of the Harmattan is as far as about 300 m above the ground level, which is beyond the stratospheric region of the atmosphere. As a matter of fact, the transportation and deposition of the Sahara dust affect the Earth's radiation budget (Bryant et al. [8], Su et al. [9], Tegen et al. [10]), which occurs naturally (Kalu [11], Falaiye et al. [12], Adimula [13], Falaiye et al. [14]) and Photolysis rates, Washington et al. [6]. This dust settles on open sun-dried agricultural products meant for human consumption, Resch et al. [15]. The thickness of the deposition of Harmattan dust on the ground surface ranged from 0.5 μ m to 1.5 μ m in 2002 and 2005 Harmattan seasons, respectively, Resch et al. [15]. Also, these dust particles constitute pollution of the air inhaled by humans and animals during respiration. The Harmattan dust deposits fine particles on different exposed objects, for example: soil, cloths, skin, buildings, ... etc. in different quantities. Studies have shown that Harmattan dust transportation has an effect on the wind patterns, Engelsaedter et al. [4], Brooks and Legrand [5], Sunnu et al. [16]. There is accumulation of the dust in the atmosphere due to climate change and largescale weather features including the Inter Tropical Convergence Zone (ITCZ) 2

(Engelsaedter *et al.* [4], Brooks and Legrand [5], Sunnu *et al.* [16], Sunnu *et al.* [17], Bryant *et al.* [8], Tegen et al [10], Goudie [18], De Longueville *et al.* [19], Sunnu [20], Ginoux *et al.* [21], Rodriguez *et al.* [22], Ravi *et al.* [23], Okin *et al.* [24], Prospero *et al.* [25], He *et al.* [26], McFiggans *et al.* [27], Breuning-Madsen and Awedzi [28]).

Studies have shown that the impacts of Sahara dust are related to climate-oriented effect, vis-à-vis physical properties of the dust, Sunnu et al. [17]. Harmattan dust has been identified as an important component in the global radiation balance (Rodriguez et al. [22], Ravi et al. [23], Okin et al. [24], Prospero [25], He et al. [26], et al. McFiggans [27]). The optical characterization of the dust shows that dust is comprised of organic compounds, which are as a result of the anthropogenic activities of the locality. In this study, the FT-IR analysis and UV characterization of suspended Harmattan dust across Sub-Sahara region of Africa monitored in 2015/2016 season were conducted to determine the characterization, functional groups and visible range of dust across the selected stations in Nigeria.

Materials and Method

(a) Sample Collection

Total suspended dust particles by sedimentation were collected by means of distilled water of about 10 liters in a Jar $(0.05x0.05x0.05 m^3)$, with the jar placed at about 10 m above the ground level, both in commercial and residential areas. The residential areas in Nigeria are such places where people reside with some little commercial activities. While, commercial areas in Nigeria are places where businesses activities, such as selling and buying, general trading, storing goods and provision of services take place. The jar was

mounted on the top of the building in order to allow the dust sample fall inside the container. See Fig. 2. For this research, a direct deposition method of suspended Harmattan sample collection was preferred; this accounts for the optical characterization and the Fourier Transformation Infrared analysis intended. During sample collection, different measures were set in place so as to prevent local dust from affecting the results, as used by Falaiye and Aweda [2], Falaiye et al. [12], Falaiye et al. [14], Aweda et al. [33]. The collection process took place at ten different stations in Nigeria, see Figs. 3 and 4.

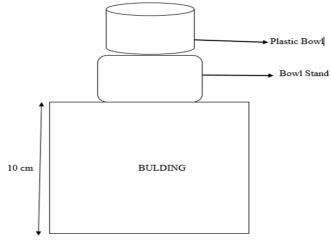


FIG. 2. Schematic structure of the experimental setup.

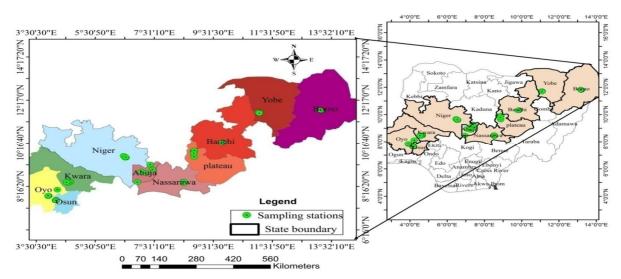


FIG. 3. Map of Nigeria showing sampling sites.

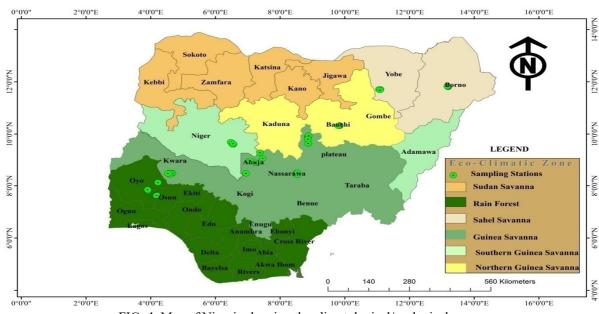


FIG. 4. Map of Nigeria showing the climatological/ecological zones.

(b) Sample Preparation and Machine Model

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(i) Fourier-Transform Infrared Spectroscopy (FT-IR) Sample Preparation

The sample collected at each location was taken to the laboratory for analysis using Fourier Transform Infrared Machine (FT-IR) manufactured by Agilent Technologies with the model number CARY 630 FTIR. The sample liquid each of about 20 ml was stirred vigorously using an electric stirrer, then a little quantity of the sample was dropped on the sensor part of the machine, then the spectra of the samples were generated. This method followed what was revealed by (Falaiye and Aweda [2]).

(ii) Preparation of UV Samples

The sample collected at each location was taken to the laboratory for analysis using Ultraviolet (UV) machine with model number UV-1800 Spectrophotometer machine of serial number A114550 manufactured by USA, Inc., 50196 with measuring mode of absorbance. The machine was used to determine the peaks of different samples collected at different stations. The samples were analyzed using standard wavelength range of 200 to 8000 (nm) with a scan speed of 0.5 m/s. The sample liquid of about 2 ml properly mixed using an electric stirrer was dropped at the sensor part of the machine, then the spectra of the samples were spectra determine generated. The were standardized with the waveband standard in order to determine the peak of each spectrum.

Results and Discussion

(a) Analysis of Harmattan Dust Haze

The FT-IR spectra measurement of Harmattan dust is shown in Figs. 5 - 10 below. The spectra peaks show the transmittance waveband from 3337.8 cm⁻¹ to 3291.2 cm⁻¹ corresponding to the Hydroxyl group, H-bonded OH stretch in plane and out of plane bonds for all the stations considered (see Table 1). These bonds may be due to the N-H and O-H stretch in plane and out of plane bonds. The stretch around 1680 – 1620 cm⁻¹ implies Akene group / Olefinic group with the stretch bond of C=C, also present across all the stations considered. The spectra peaks between 1981.1 – 2119.9 cm⁻¹ indicate C-C bond. This bond represents the presence of transition metals and unsaturated bond found in the samples. The transition metals include K, Ca, Ti, Mn, Fe, Ni, Cu, Zn, Mo, As, Zr, Pb, V, Sr, Cr and Ce. This supports the fact that FTIR can also be used to determine transition metal elements present in suspended Harmattan dust. The broad peaks around 3700 - 3000 cm⁻¹ are due to O-H stretch which corresponds to the hydroxyl groups. More so, the peak range from 1300-700 cm⁻¹ shows the skeletal C-C vibrations or Aromatic C-H plane bond which is also known as Aliphatic Flouro compound C-F bond stretch present in the samples collected across the stations. This may be due to smoke from machines. However, the stations such as Ilorin, Lafia and Potiskum have the peak range of 1015.7 cm⁻¹ which may be due to P-O-C stretch Aliphatic Phosphate present in the samples collected at these stations as a result of road construction taking place at these stations, as reported by Cameron [29].

The FTIR measurement of nickel ferrite nanorods (NF NR) at room temperature through the wave range 400 - 4000 cm⁻¹ is as shown in Figs. 3 and 4. The stretch for NF NR was at 420.48 cm⁻¹ which corresponds to the metal-oxygen bonds due to Ni - O and Fe - O. This is in good agreement with Coates [30]. The peak at 1068.56 cm⁻¹ which was found to be around 1260–1050 cm⁻¹ gives cyclohexane ring vibration, C-F stretching, C-O stretching alcohols, carboxylic acids, esters and ethers (Cameron, [29]).

The peaks between 1537.80-1500.31 cm⁻¹ indicate O-H in-plane and out-of-plane bonds and appeared at 1512.19 cm⁻¹. The peak at 1357.89 cm⁻¹ indicates aliphatic nitro compound, methyne C-H bending. The peaks around 3700 - 3000 cm⁻¹ were observed at 3452.58 cm⁻¹ leading O-H which corresponds to the hydroxyl groups attached by the hydrogen bonds to the iron oxide surface and the water molecules chemically adsorbed to the magnetic particle surface (associated water content).

However, the FTIR spectra of suspended Harmattan dust, as shown in Figs. 5 - 14, have transmittance waveband ranging from 42.745 cm⁻¹ to 96.863 cm⁻¹, which corresponds to the metal-oxygen bonds (Coates, [30]). This is in

good agreement with Kandasamy et al. [31]. The spectra peaks between 1529.55-1500.31 cm⁻¹ and 1260-1031.92 cm⁻¹ indicate O-H in-plane and out-of-plane bonds, respectively. The broad peaks around 3700 - 3000 cm⁻¹ are due to O-H stretch which corresponds to the hydroxyl groups which had been completely removed when the sample is sintered at temperatures \geq 973K, as reported by Dev and Ghose [32]. Hence, the FTIR analysis confirmed the formation of the suspended Harmattan dust samples in the atmosphere across the country. However, Figs. 5 and 6 (Oyo and Iwo) are almost similar, because the two statins are located in the western part of the country. These two stations are less than 50 km by land travel to each other. Moreover, they are located in different states.

(b) Mineralogical Composition of Harmattan Dust Using FTIR Spectrum

Figures 5 - 14 also show the quantitative analysis carried out on the liquid samples collected across all the stations considered for this research. This analysis was carried out to determine the major and minor constituent minerals present in the samples collected across the stations from the band position of the peaks from the prominent FTIR absorption peaks. These minerals were identified with the available literature to determine the quantities present in the samples collected across the stations.

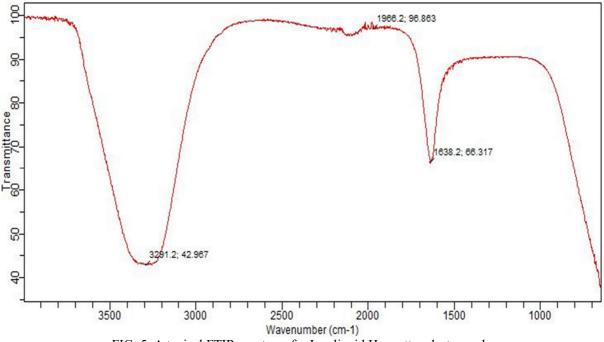


FIG. 5. A typical FTIR spectrum for Iwo liquid Harmattan dust sample.



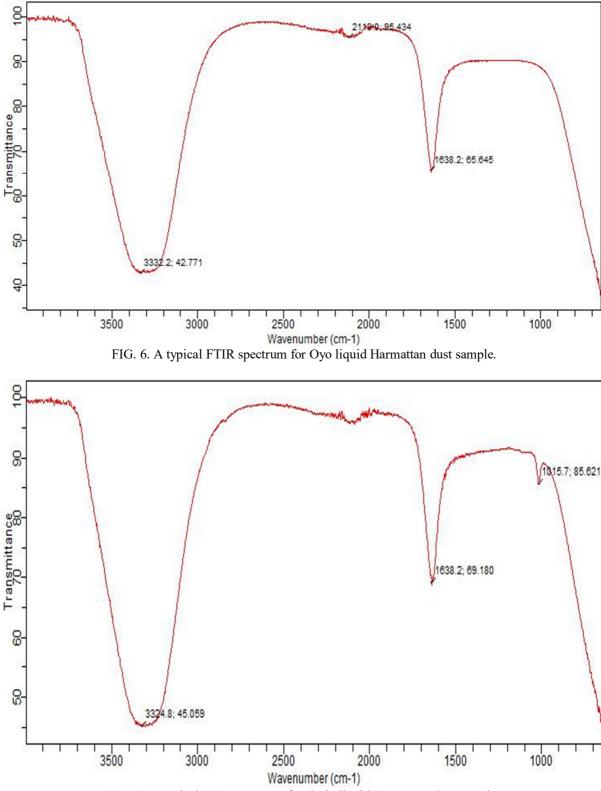
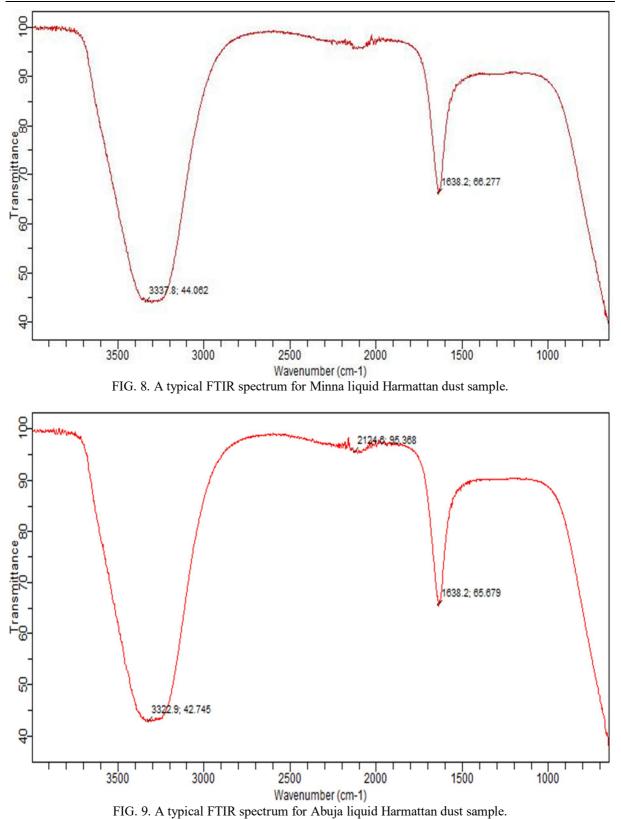
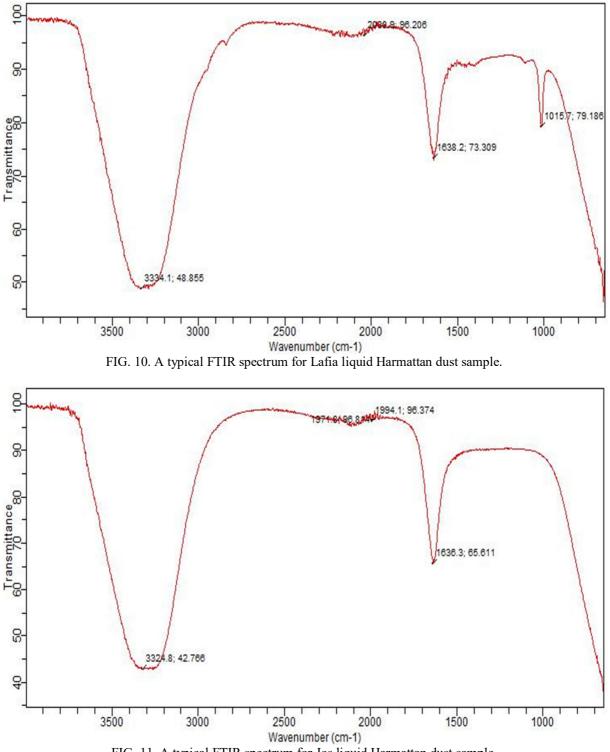
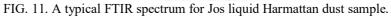


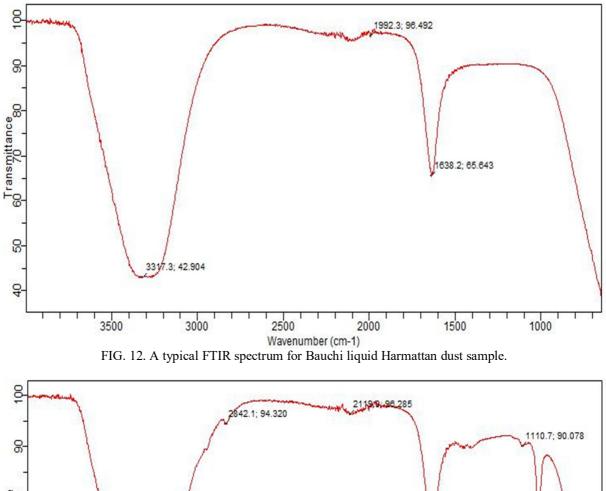
FIG. 7. A typical FTIR spectrum for Ilorin liquid Harmattan dust sample.







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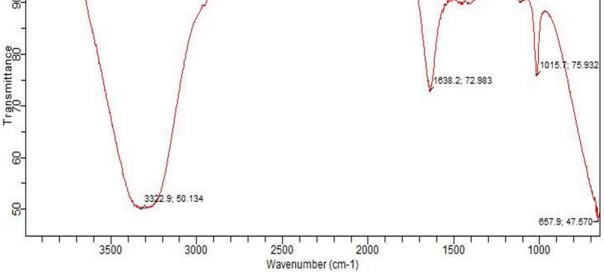


FIG. 13. A typical FTIR spectrum for Potiskum liquid Harmattan dust sample.

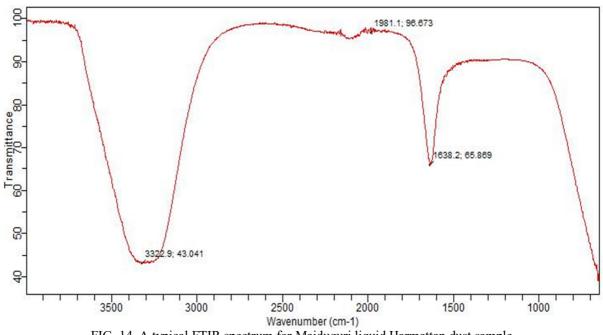


FIG. 14. A typical FTIR spectrum for Maiduguri liquid Harmattan dust sample.

From the above Figures, it can be seen that all the ten spectra present distinct peaks in the following ranges: $32091.2 - 3337.8 \text{ cm}^{-1}$, $1966.2 - 2124.6 \text{ cm}^{-1}$, $1636.2 - 1638.2 \text{ cm}^{-1}$, $1015.7 - 1015.7 \text{ cm}^{-1}$, 19719 cm^{-1} , 2842.1 cm^{-1} and 1110.7 cm^{-1} . The broad and strong band situated in the range $3291.2 - 3337.8 \text{ cm}^{-1}$ can be attributed to overlapping of -OH and -NH stretching. The band from the range $1600 - 1400 \text{ cm}^{-1} \text{ C} = \text{C}$ alkene is weak. The band from $1015.7 - 1077 \text{ cm}^{-1}$ was assigned to the CO stretching of alcohols and carboxylic acid. More so, the figures show that the stations are located in Nigeria, since the latitude of the country is 4^0N located at western Africa.

(c) Composition of Quartz Mineral Using FTIR Spectrum

Quartz was observed to be the commonest of all the rocks forming minerals which are also most important constituent of the earth crust. It is also observed to be the second most abundant mineral in the earth's crust. Chemically, it is represented as silicon oxide, SiO₂. It occurs in crystals of the hexagonal shape which makes it to be commonly terminating in a six-sided pyramid. Quartz is a common constituent of granite sandstone, limestone and many other igneous, sedimentary and metamorphic rocks. As can be observed from Figs. 5 - 14, the FTIR absorption band appearing at 1638.2cm⁻¹, 1015.7 cm⁻¹ may suggest the presence of quartz in the samples. The bending vibration at 1971.9 cm⁻¹ and the symmetrical stretching vibration at 1992.3 cm⁻¹ are assigned, where the pattern of absorption in quartz can be explained by ascribing the 1971.9 cm⁻¹ region (Si-O asymmetrical bending vibration), the band region 1994.1 cm⁻¹(Si-O symmetrical bending vibrations) and the bands in the region 1966.2 cm⁻¹ (Si-O symmetrical stretching vibration).

(d) Composition of Clay Minerals Using FTIR Spectrum

It was observed that the presence of kaolinite, illite and montmorlinte indicated clay mineral in the samples collected across all the locations. Kaolinite is said to be a clay mineral in crystallization which occurs in the monoclinic system and forms the major constituent of Nigeria clay. As can be observed from Figs. 5 -14, the FTIR absorption peaks appearing at 1015.7 cm⁻¹ in the samples indicate kaolinite. Absorbance at 1030 cm⁻¹ is attributed to Si-O stretching of clay minerals.

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UV/VIS Characterization and FT-IR An	nalysis of Harmattan Dust across	Sub-Sahara Region of Africa

ABLE I. Different compound groups and frequencies of Harmattan dust.				
Station	Origin	Group frequency Wavenumber (cm ⁻¹)	Functional Group	
Iwo	O-H	3400-3200	Normal polymeric OH Stretch	
	C=C	1680-1620	Alkenyl C=C Stretch	
	-NCS	2150-1990	Isothiocyanate	
	O-H	3400-3200	Normal polymeric OH Stretch	
Оуо	C=C	1680-1620	Alkenyl C=C Stretch	
	-SCN	2175-2175	Thiocyanate	
	O-H	3400-3200	Normal polymeric OH Stretch	
Ilorin	C=C	1680-1620	Alkenyl C=C Stretch	
	C-F	1150-1000	Aliphatic fluoro compounds C-F stretch	
Minus	O-H	3400-3200	Normal polymeric OH Stretch	
Minna	C=C	1680-1620	Alkenyl C=C Stretch	
	O-H	3400-3200	Normal polymeric OH Stretch	
Abuja	-NCS	2150-1990	Isothiocyanate	
-	C=C	1680-1620	Alkenyl C=C Stretch	
	O-H	3400-3200	Normal polymeric OH Stretch	
т.с.	C≡C	2200-2000	Cyanide ion, thiocyanate ion and related ion	
Lafia	C=C	1680-1620	Alkenyl C=C Stretch	
	P-O-C	1050-990	Aliphatic Phosphate	
	O-H	3400-3200	Normal polymeric OH Stretch	
Jos	-OCN and C-OCN	2285-1990	Cyanates, Isocyanates, Thiocyanate	
	C=C	1680-1620	Alkenyl C=C Stretch	
	O-H	3400-3200	Normal polymeric OH Stretch	
Bauchi	C=C	1680-1620	Alkenyl C=C Stretch	
	-NCS	2150-1990	Isothiocyanate	
	O-H	3400-3200	Normal polymeric OH Stretch	
	О-СН ₃ , С-Н	2850-2815	Methoxy, Methly	
Potiskum	-OCN and C-OCN	2285-1990	Cyanates, Isocyanates, Thiocyanate	
rouskum	C=C	1680-1620	Alkenyl C=C Stretch	
	C-O-C	1150-1050	Alkyl	
	P=O	1100-1000	Phosphate ion	
	О-Н	3400-3200	Normal polymeric OH Stretch	
Maiduguri	-NCS	2150-1990	Isothiocyanate	

 TABLE 1. Different compound groups and frequencies of Harmattan dust.

Table 1 above presents the results of all the stations observed in terms of compound group and frequency of the suspended Harmattan dust across Nigeria.

It was observed that all the stations presented have O-H broad band of group frequency wavenumber range 3400-3200 cm⁻¹, with normal polymetric OH stretch. This shows that alcohols and hydroxyl compounds are present in the dust samples collected. As reported by Coates [30], hydroxyl functions are most dominant characteristics of all the infrared group frequencies. These compounds were found in all the stations, which shows peculiar characteristics of the dust in Nigeria. Due to known facts, in most chemical environments, the hydroxyl group

does not exist in isolation and a high degree of association is expressed as a result of extensive hydrogen bonding with hydroxyl group, Coates [30].

Furthermore, Table 1 shows that the C=C bonds present in the samples collected across stations are of different magnitudes and this may be dependent on the nature of the topography in the various areas considered. The group frequency wavenumber range 1680-1620 cm⁻¹ C=C bond was found to be present in the stations (Alkenyl C=C Stretch).

As reported by Coates [30], the position of the C=C stretching frequency does not vary slightly as a function of orientation around the

double bond, but it's less informative than the C-H information. However, a fully substituted medical double bond has only the C=C as the sole indicator of the presence of the double bond, unless the bond is conjugate with a second unsaturated site, Coates [30].

As shown in Table 1, -NCS (Isothiocyanate) observed in the samples was present in Iwo, Abuja, Bauchi and Maiduguri, falling in the group frequency range 2150-1900 cm⁻¹. –NCS (Isothiocyanate) was not present in other stations.

Thiocyanate (-SCN) of group frequency range 2175-2140 cm⁻¹ was found to be present in Oyo, due to some background activities taking place around the station. Thiocyanate is a multiple bonded nitrogen compound, Coates [30].

The C-F bond was observed in Ilorin, which is likely to be due to the emissions from neighboring pharmaceutical companies. The C-F is an aliphatic fluoro-compound, which stretches with group frequency wavenumber range 1150-1000 cm^{-1} . P-O-C (Phosphorus Oxy _ compounds) were only present in Lafia, Nasarawa State of Nigeria, but not present in other stations. P-O-C is aliphatic phosphate (P-O-C stretch) with the group frequency range 1050-990 cm⁻¹. Methoxy, methyl (O-CH₃) and C-H stretch were observed to be present in Postiskum area, but not present in other areas, probably due to the density of these compounds. Methyl has the group frequency range of 2850- 2815 cm^{-1} .

UV Optical Characterization of Harmattan Dust

The ultraviolet (UV) and visible regions of the electromagnetic spectrum of the Harmattan dust collected across stations cover the wavelength range from about 100 nm to about 800 nm. The visible region occurs between 400 nm and 800 nm as reported by Kealey and Haines [34]. However, from the UV-vis characterization, the samples (Harmattan durst hazes) strongly absorb UV light and weakly absorb visible light. Figs. 15 - 24 show the absorbance spectra of the samples. All have maximum UV absorbance peaks at around 210 nm wave band and weak visible light absorbance peaks (orange - red spectra) around 620 nm and 700 nm.

This shows that the Harmattan dust haze could have minimal advantages in relation to UV radiation protection. However, the orange - red spectral absorbance shows that it could trap visible light radiations from the sun and hence reduce the greenhouse effect. This is a confirmation of the presence of greenhouse gases or substances having some chemical compositions as contained in greenhouse gases as shown by the EDS and FTIR analyses. This report is in agreement with Falaiye et al. [12], Falaiye and Aweda [2], Aweda et al. [33], who worked on elemental composition of Harmattan dust haze collected by dry method and found that elements, such as Ca, Na, Mg, Mn and Cu, are in the visible range of the atmosphere.

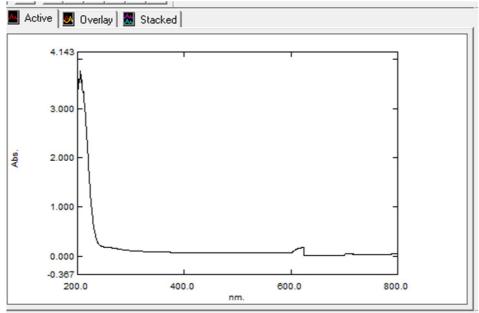


FIG. 15. A typical UV spectrum for Iwo liquid Harmattan dust sample.

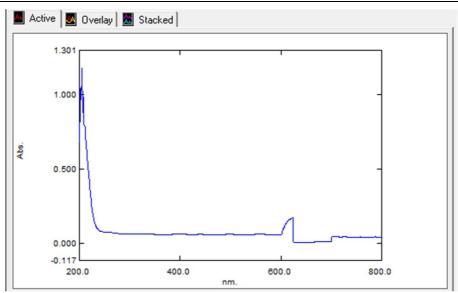


FIG. 16. A typical UV spectrum for Oyo liquid Harmattan dust sample.

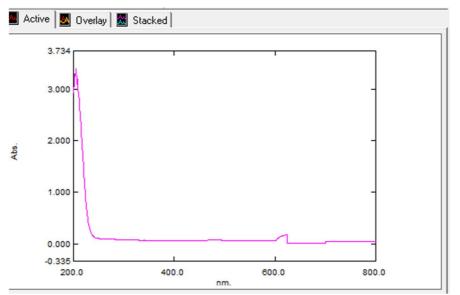


FIG. 17. A typical UV spectrum for Ilorin liquid Harmattan dust sample.

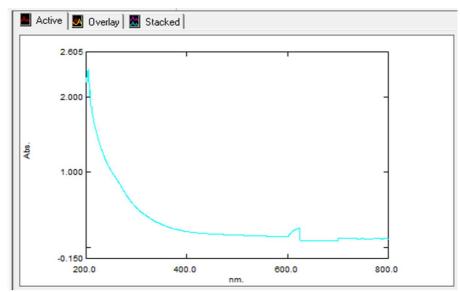
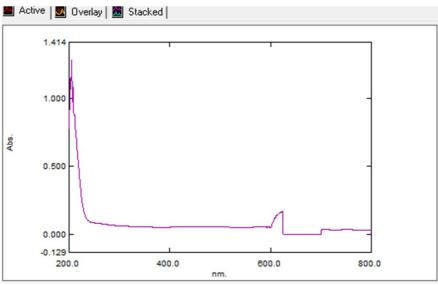


FIG. 18. A typical UV spectrum for Minna liquid Harmattan dust sample.





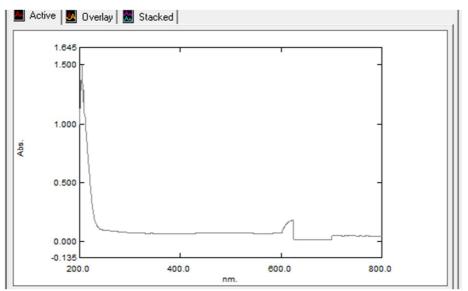


FIG. 20. A typical UV spectrum for Lafia liquid Harmattan dust sample.

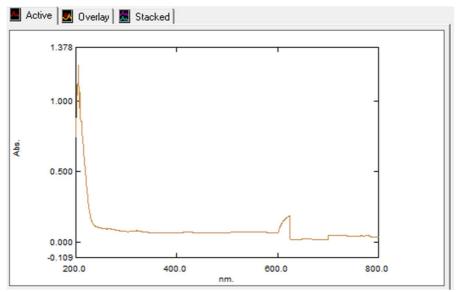


FIG. 21. A typical UV spectrum for Jos liquid Harmattan dust sample.

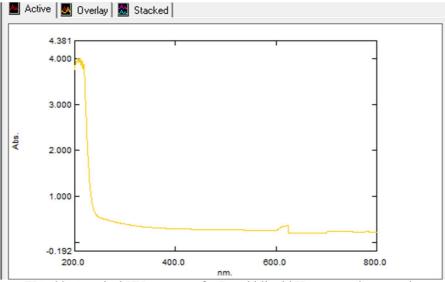


FIG. 22. A typical UV spectrum for Bauchi liquid Harmattan dust sample.

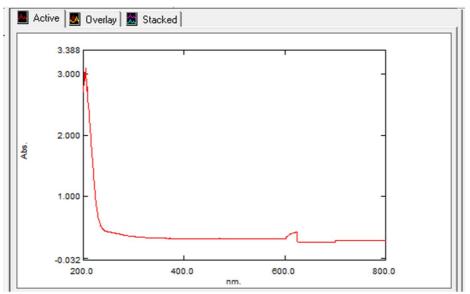


FIG. 23. A typical UV spectrum for Potiskum liquid Harmattan dust sample.

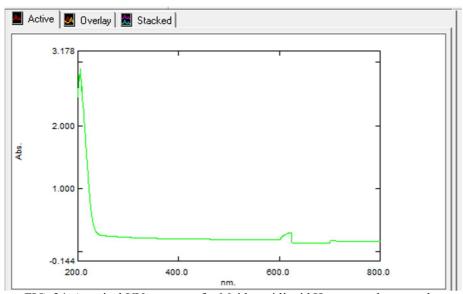


FIG. 24. A typical UV spectrum for Maiduguri liquid Harmattan dust sample.

The spectral absorption measurements for the stations under consideration indicate greater relative absorption in the UV (350 nm) than in visible or near infrared wavelengths for the large particles but smaller UV effects are found for small aerosol in stations like Lafia, Iwo, Maiduguri, Oyo, Bauchi, Ilorin, Abuja, Potiskum and Minna, with Jos having relative absorption below the UV range. The aerosol in all the stations has interactions with the UV radiation field, decreasing the UV spectral transmittance. These aerosols were primarily dust particulate matters, with trace quantities of heavy metals. These occupied partly d of f orbitals often showing absorption bands in the visible region and these are affected by the bounding of ligands, Kealey and Haines [34].

Conclusion

Minerals, such as quartz, microcline, kaolinite ... etc. and some elements are present in the suspended Harmattan dust. Among these minerals, quartz is the major mineral detected using FTIR peaks, whereas minerals, such as clay, are found to be minor minerals. The accessory minerals are found to be kaolinite

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from the study of the FTIR machine. The FTIR approach is tremendous due to its non-acidic dissolution of the samples used. However, in this present study, the FTIR screening confirmed the presence of thirteen (13) functional groups: Normal polymeric (O-H), Alkenyl (C=C), Isothiocynate (-NCS), Aliphatic fluoro compounds (C-F), Cyanide ion (C≡C), Thiocyanate ion (-SCN), Aliphatic phosphate (P-O-C), Cyanate (-OCN), Isocyanates (C-OCN), Methoxy (O-CH₃), Methly (C-H), Alkyl (C-O-C) and Phosphate ion (P=O) in suspended Harmattan dust collected across Nigeria. This is a result of heavy dust that blows from the Sahara. More so, the UV/VIS screening revealed that light can penetrate particles at lowfrequency range. The minerals and elements detected in the samples collected across the ten locations selected varied with different concentration values as a result of different climatic locations of the various towns in the country. It is therefore recommended that physicochemical characterization of dust should be done parallel with or followed by biological characterization across the entire country.

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