Characterization of adsorbents from plant source (water leaf (*Talinum Triangulare*), bitter leaf (*Vernonia Amygdalina*) and vetiver grass (*Vetiveria Zizanioides)* using infrared spectrometric tecnnique

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Abstract

Powdered samples of Bitter leaf (PBL), Water leaf (PWL) and Vetiver grass (PVG) were analyzed with the use of Nicolet IS5 Fourier Transform Spectrometer to identify the functional groups present in these plants. Results obtained showed the presence of alcohol (OH), alkane (C-C) and alkene (C=C) in all three plants as indicated by the peaks at wavelength ranges of 3600 - 3200cm^{-1}, 2935 - 2915cm^{-1} and 1680- 1620cm^{-1} respectively. Tertiary alcohol and phenol were also present in all three plants as indicated in the wavelength ranges of 1420 - 1330cm^{-1} and 1390 - 1310cm^{-1} respectively. Carbonyl (C=O) and Nitro (N=O) functional groups were exclusively found in Bitter leaf at wavelength ranges of 1740 - 1715cm^{-1} and 1550 - 1500 cm^{-1} respectively while wavelength ranges of 1190 - 1130cm^{-1} and 1090 - 1020cm^{-1} indicates the presence of secondary and primary amines exclusively present in Bitter leaf and Vetiver grass. Functional groups such as sulfoxide (S=O) and iodo compounds (C-I) as indicated at wavelength ranges of 1070 - 1030cm^{-1} and 600 - 500cm^{-1} were present in Vetiver grass. The higher the molecular polarizability of the plants which is a function of the polar functional groups present, the higher the adsorption capacity of the plant. The presence of carbonyl functional groups in Bitter leaf will give it an advantage in terms of adsorption capacity compared to Water leaf and Vetiver grass because carbonyl functional groups are highly polarized due to their ability to form hydrogen bond as well as the presence of high dipole moments orchestrated by two electronegative atoms.

Keywords: Electronegativity, polarizability, wavelength, adsorption, functional group, spillage, spectrum.

Introduction

The discovery of crude oil as well as the continuous exploration and transportation of the natural resource in various nations of the world has exposed the environment to different degrees of spillage. The growth and consumption of crude oil worldwide has led to increase in its exploration and other anthropogenic activities related to its production consequently resulting to the consistent release of the product thereby polluting the land, water sources as well as the atmospheric environment[1]. In Niger Delta, Nigeria, the major causes of oil spillage are pipeline vandalization by persons or groups seeking the attention of government to adequately address the ecological catastrophe and economic marginalization orchestrated by many years of unregulated crude oil exploitation and exploration by international and local oil companies in the Niger Delta[2]. Current statistics on oil spills collected by the National Oil Spill Detection and Response Agency (NOSTRA) estimated that Nigeria has recorded 6,673 oil spill incidence which released 250,973.96 barrels of oil resulting in very serious challenges in the environment especially in the Niger Delta region between 2009 till date, of which over 53% is directly connected to human activities including intentional waste disposal and act of sabotages and vandalization[3].

Various clean up techniques are employed to protect and maintain the integrity of the environment however one of the basic principles in the treatment of oil spillage is Adsorption. Adsorption is the attachment of atoms, ions or molecules from matter to a surface. Adsorption is different from absorption because it is a surface phenomenon unlike the latter which involves the entire material volume. The process of adsorption creates an adsorbate (liquid material) film on the surface of the adsorbent (solid)[4]. There are basic factors to consider while choosing adsorbents in the cleanup of oil spillage ranging from the ability of the adsorbents to attract ions, atoms or molecules to its surface to the environmental friendliness of the adsorbents after clean up especially during disposal[5]. Apart from the cost effectiveness of adsorbents of plant origin they are also easily biodegradable with a high level of remediation abilities (restore the ecosystem to its original state). Plants such as Water Leaf (*Talinum Triangulare*), Bitter Leaf (*Vernonia Amygdalina*) and Vetiver Grass (*Vetiveria Zizanioides)* have been used over the years to clean up oil spillage through phytoremediation based on their unique characteristics[6,7]. It has been recorded that waterleaf reduces the Total petroleum hydrocarbon (TPH) of an oil contaminated soil reasonably up to 28%[8] while Vertiver Grass can be used to purify polluted sites and normalize the eutrophic areas, In addition they are also involved in translocation

processes that is the uptake of contaminant using plants roots through phytoextraction[9,10]. Agwaramgbo *et al*. showed that bitter leaf can reduce the Total petroleum hydrocarbons of an oil contaminated soil by 61%, however there has not been much research on the usage of bitter leaf in phytoremediation of crude oil spills[11,12]. The pictures of bitter leaf, water leaf and vetiver grass are shown in Figures-1, 2 and 3 respectively.

One of the active ingredients that determines the adsorption characteristics of adsorbents is the functional group which is basically identified with the use of Infrared Spectrometric Technique. The influence of functional groups on adsorption is dependent on the relationship of its influence on molecular polarizability and adsorbate-adsorbent interactions. Generally, increase in polarizability is directly proportional to increase in the volume occupied by electrons because larger atoms have more loosely bound electrons compared to smaller atoms[13]. The aim of this study is to characterize Water Leaf (*Talinum Triangulare*), Bitter Leaf (*Vernonia Amygdalina*) and Vetiver Grass (*Vetiveria Zizanioides)* using Infrared Spectrometric technique to ascertain the functional groups in the plant hence creating an avenue to anticipate other plants with similar characteristics which can be deployed for similar purpose.

Materials and methods

Sample collection and preparation: Water Leaf (*Talinum Triangulare*), Bitter Leaf *(Vernonia Amygdalina)* and Vetiver Grass (*Vetiveria Zizanioides*) were collected locally from a farm at Choba, port Harcourt, Rivers state. The leaves were properly washed with normal water and then de-ionized water to remove dust, soil and other particles. The leaves of the plants were plucked out separately and air dried for 28 days. The samples were mechanically ground into fine powder separately using an agate mortar and then dried at 65^0 in an oven to obtain a constant weight and later sieved to get particles 30µm mesh for large surface area. The fine powdery particles were put into Ziploc bags and preserved prior analyses.

Fourier transform infrared (FT–IR) Characterization: Dried powder of the leaves of all three plants, water Leaf (PWL), bitter Leaf (PBL) and vetiver grass (PVG) were used for FT-IR analysis. Encapsulate 10mg of the dried extract powder of each of the plant 100mg of KBr pellet in order to prepare translucent sample discs. The powdery form of the leaves was introduced in FT-IR spectroscope with a Scan range from 400 to 4000cm^{-1} with a resolution of 4cm^{-1}. The powdery form of the plant and KBr disc mixture was thereafter placed in the equipment and carefully analyzed to obtain the different functional groups of the plants through the different peaks eluted on the FT-IR spectroscopic screen. The functional groups in the plant were determined by the shape and size of the peaks as well as the wavelength at which they elute[14].

Results and discussion

Table-1 shows the functional groups present in dried powdered bitter leaf (PBL) obtained by infrared spectrometric technique. These functional groups are confirmed basically by the shapes of the individual peaks as well as the wavelength at which they elute as shown in Table-1.

Table-2 shows the functional groups present in dried powdered water leaf (PWL) obtained by infrared spectrometric technique. These functional groups are confirmed basically by the shapes of the individual peaks as well as the wavelength at which they elute as shown in Table-2.

Table-3 shows the functional groups present in dried powdered vetiver grass (PVG) obtained by infrared spectrometric technique. These functional groups are confirmed basically by the shapes of the individual peaks as well as the wavelength at which they elute as shown in Table-3.

The adsorption characteristics of these plants (bitter leaf, water leaf and vetiver grass) is determined by the functional groups prevalent in them as shown in their individual infrared spectrum.

Figure-1: Bitter Leaf (Vernonia Amygdalina)[15].

Figure-2: Water Leaf (_Talinum triangulare_)[15].

Figure-3: Vetiver grass (_Vetiveria Zizanioides_)[15].

Table-1: Infrared Characteristics of Dried Powdered Bitter Leaf (PBL) Samples.

Wave number (cm⁻¹)	Group frequency (cm⁻¹)	Functional groups	Possible compounds
3289	3570-3200	H-bonded O-H stretch	Hydroxy group (Alcohol)
2918	2935-2915	Asymmetrical C-H stretch	Methylene (Alkane)
2850	2865-2845	Symmetrical C-H stretch	Methylene (Alkane)
1729	1740-1715	C=O stretch	Aldehyde, Ester
1630	1680-1620	C=C stretch	Alkenyl (Alkene)
1547	1550-1500	N-O stretch	Aliphatic nitro compound
1378	1390-1310/1420-1330	O-H bend	Phenol or tertiary alcohol
1315	1360-1250	C-N stretch	Aromatic amine
1237	1275-1200	C-O stretch	Alkyl aryl ether
1151	1190-1130	C-N stretch	Secondary amine
1020	1090-1020	C-N stretch	Primary amine

Table-2: Infrared Characteristics of Dried Powdered Water Leaf (PWL) Samples.

Wave number (cm⁻¹)	Group frequency (cm⁻¹)	Functional groups	Possible compounds
3274	3550-3200	O-H stretch	Alcohol
2918	2935-2915	Asymmetrical C-H stretch	Methylene (Alkane)
2850	2865-2845	Symmetrical C-H stretch	Methylene (Alkane)
1618	1620-1610	C=C stretch	α, ß-Unsaturated Ketone
1400	1420-1330	O-H bend	Tertiary alcohol
1318	1390-1310	O-H bend	Phenol
1097	1124-1087	C-O stretch	Secondary alcohol
892	895-885	C=C bend	Alkene

Table-3: Infrared Characteristics of Dried Powdered Vetiver Grass (PVG) Samples.

| Wave number (cm⁻¹)	Group frequency (cm⁻¹)	Functional groups	Possible compounds
3304	3500-3310	O-H stretch	Alcohol
2917	2935-2915	Asymmetrical C-H stretch	Alkanes
2850	2865-2845	symmetrical C-H stretch	Alkanes
1639	1662-1600	C=C stretch	Alkenes
1546	1500-1600	C=C stretch	Aromatic rings
1371	1420-1330	O-H bend	Tertiary Alcohol
1332	1390-1310	O-H bend	Phenol
1235	1250-1020	C-N stretch	Amine
1030	1070-1030	S=O stretch	Sulfoxide
521	600-500	C-I stretch	Aliphatic iodo compounds
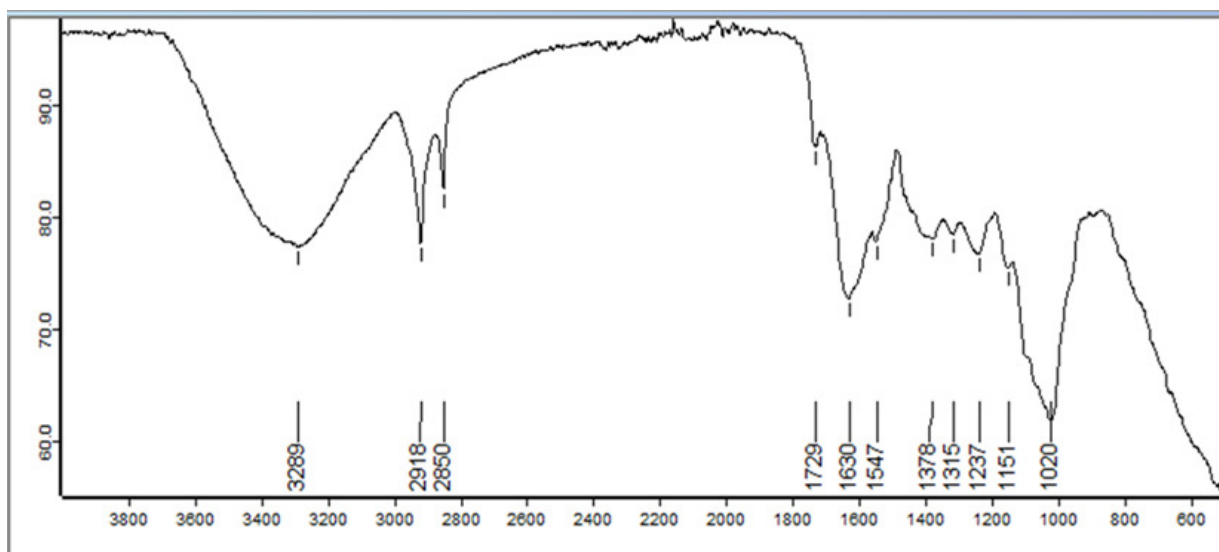
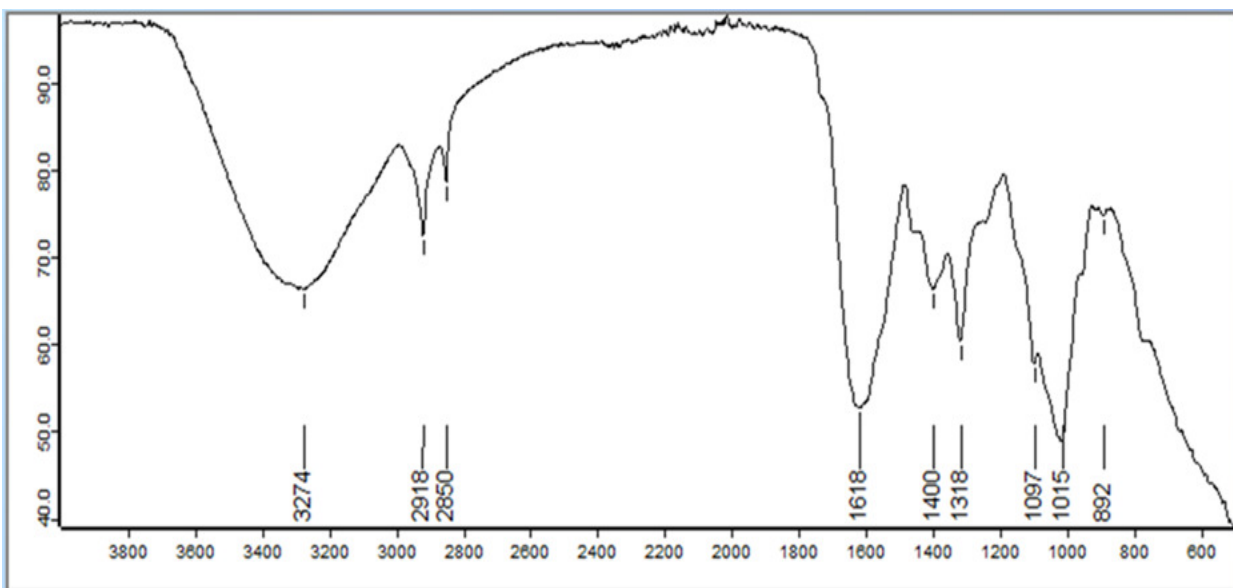**Figure-4:** FT-IR Spectrum of dry Powdery bitter leaves.

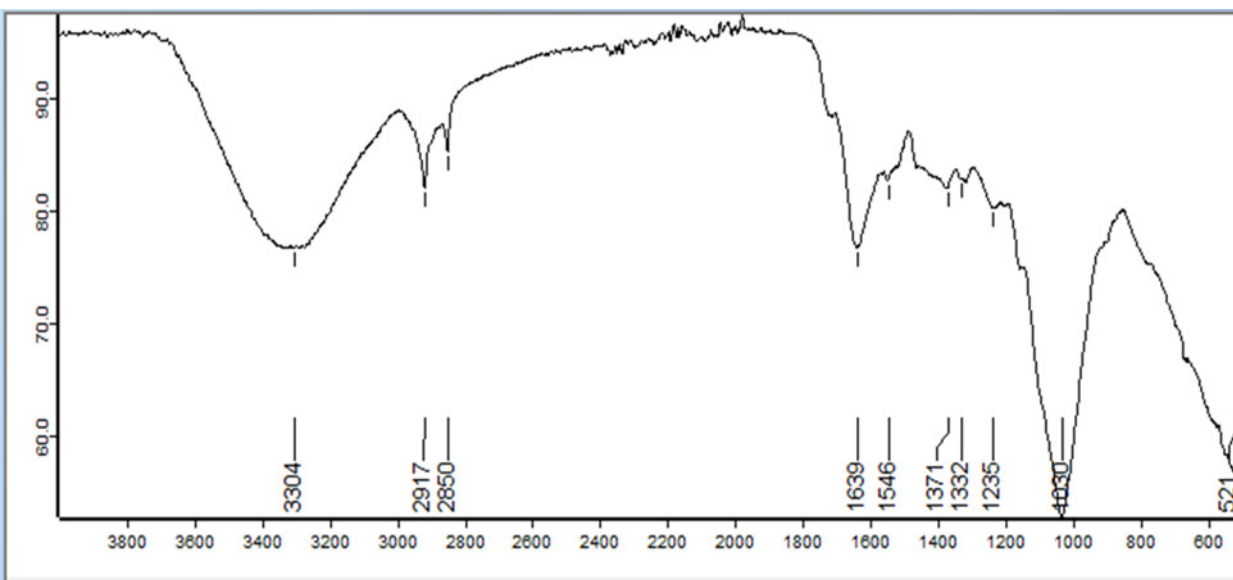**Figure-5:** FT- IR Spectrum of dry powdery waterleaf.

Figure-6: FT-IR Spectrum of dry powdery vetiver grass.

The FT-IR (Fourier transform infrared spectroscopy); is a strong technique employed in the determination of infrared spectrum of polyatomic molecules. The FT-IR spectroscopy helps in the determination of the shapes, structure, biological and chemical properties of the plant leaves. It is perhaps the most powerful tool for identifying the types of functional groups and chemical bonds present. The most noticeable feature of the chemical bond shown on the annotated spectrum is obtained through the wavelength of light absorbed. The interpretation of the infrared absorption spectrum determines the chemical bonds in a compound[16]. The peaks, primary assignments (functional groups) and possible compounds present in powdered bitter leaves (PBL) as illustrated in Figure-4 are shown in Table-1. The spectrum of the graph from Figure-4 shows various peaks

in the absorbance versus wavelength relationship. Infrared Spectrometric analyses of dried powdery bitter leaves revealed peaks at 3289, 2918, 2850, 1729, 1630, 1547, 1378, 1315, 1237, 1151, and $1020cm^{-1}$. The result of the FT-IR spectroscopy shows the presence of 11 functional groups, the expected phyto compounds and confirms the presence of various chemical constituents such as alcohol, aliphatic nitro compounds, alkanes, aromatic amines, primary and secondary amines, phenol, aldehyde, ester, and alkyl aryl ether in bitter leaf. The strong instance peaks are identified at 3329, 2918, 1630 and $1020cm^{-1}$. They are assigned to H-bonded, O-H stretch, C-H stretch, C=C stretch and C-N stretching vibrations respectively and its shows the presence of alcohol, alkane, alkene and primary amine in the leaves of bitter leaf. The peaks at 1315 and $1151cm^{-1}$ are

assigned to aromatic and secondary amines which confirms that amino compounds are present in the leaves of bitter leaf. Some other groups such as methylene (Alkane), aldehyde, aliphatic nitro compound, phenol or tertiary alcohol, alkyl aryl ether are absorbed at 2850, 1729, 1547, 1378, and 1237cm^{-1} respectively[17].

The peaks, primary assignments (functional groups) and possible compounds present in powdered waterleaf (PWL) as illustrated in Figure-5 are shown in Table-2. Infrared Spectrometric analyses of dried powdery water leaves revealed peaks at 3274, 2918, 2850, 1618, 1400, 1318, 1097, 1015 and 892cm^{-1}. The infrared spectrum (IR) spectrum of dry leaves of waterleaf unveils analyzable information about major and minor constituents. The peak at 3274cm^{-1}, 1400cm^{-1} and 1318cm^{-1} assigned to the O-H stretching vibration, O-H bending vibration and O-H bending medium vibration respectively shows that some alcoholic compounds are present in the leaf extracts. The strong narrow peak at 2918cm^{-1} and the narrow week peak at 2850cm^{-1} represents asymmetric C-H stretch (methylene) alkane and symmetric C-H stretch (methylene) alkane respectively. The strong peak intensity at 1619cm^{-1} represents strong C=C skeletal stretching of unsaturated ketone while the strong peak intensity at 1015cm^{-1} represents the presence of primary alcohol. Presence of C=C and C-O bonding structures at peaks 897cm^{-1} and 1097cm^{-1} respectively confirms the presence of alkenes and secondary alcohols[18].

The peaks, primary assignments (functional groups) and possible compounds present in powdered vetiver grass (PVG) as illustrated in Figure-6 are shown in Table-3. Infrared Spectrometric analyses of dried powdery vetiver grass revealed peaks at 3304, 2917, 2850, 1639, 1546, 1371, 1332, 1235, 1030, and 521cm^{-1}. The IR spectrum of vetiver grass as shown in Figure 6 shows the presence of peak at 3304cm^{-1} which corresponds to O-H stretching vibration representing alcohols, peaks at 2917cm^{-1} and 2850cm^{-1} which represents asymmetrical and symmetrical C-H stretch respectively and are assigned to Alkanes. The absorption peaks at 1639cm^{-1} and 1546cm^{-1} are due to C=C stretch which are assigned to alkenes and aromatic rings respectively. The peaks at 1371cm^{-1} and 1332cm^{-1} attributed to O-H bend are assigned to phenol and alcohol groups. The sharp peak at 1030cm^{-1} corresponds to S=O stretch for sulfoxide and lastly peak at 521cm^{-1} for C-I stretch is assigned to aliphatic iodo compounds[14].

Conclusion

The use of plants in the remediation of crude oil contaminated environment has been an age long practice however little effort has been employed in determining the functional groups responsible for the adsorption characteristics of these plants. Identification of the functional groups in powdered bitter leaf, water leaf and vetiver grass unveiled the presence of alcohols (OH$^-$), Alkanes (C-H) and Alkenes (C=C) in all three plants. Vetiver grass and bitter leaf contains primary amines with bitter

leaf having additional aromatic and secondary amines. Other functional groups exclusively found in bitter leaf are the carbonyl functional groups (C=O) which gives rise to aldehydes, ketones, esters etc. The impact these functional groups have in the adsorption characteristics of the plants is dependent on their influence on the plants' molecular polarizability as well as the adsorbate – adsorbent interactions.

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