

ADSORPTION OF HERBICIDE, GLYPHOSATE, 2- [(PHOSPHONOMETHYL) AMINO] ACETIC ACID ONTO LOCALLY DERIVED ADSORBENT: AN FTIR - GCMS APPROACH IN QUALITATIVE ANALYSIS

Itodo A.U.^{1*}, Adetunji I.I.², Itodo H.U.³, Gafar M.K.⁴, Usman A.⁵

¹Department of Chemistry, University of Agriculture, Makurdi, Nigeria

²Department of Applied Chemistry, Kebbi State University of Science and Technology, Aliero, Nigeria

³Environmental Chemistry Unit, University of Agriculture, Makurdi, Nigeria

⁴Department of Chemistry, Federal University Dutsinma, Katsina State, Nigeria.

⁵Basic Science Unit, Nasarawa State University Keffi, Shabu-Lafia Campus, Keffi, Nigeria

ABSTRACT. The adsorption of unsuspected pollutant, an organo-phosphorus herbicide with the general name; glyphosate, trade name; Roundup and chemically called 2-[(phosphonomethyl) amino] acetic acid or N-(phosphonomethyl) glycine was qualitatively investigated. A batch adsorption mode was utilized as reactor in interacting herbicide solution with derived activated carbon. Results obtained from FTIR and GCMS run revealed the phenomenon likened to the adsorption of certain functional groups from the herbicide viz; NH-Amine (peak range of 3300-3500 cm^{-1}), polyoxyethyleneamine in glyphosate herbicides, CO Carbonyl groups (3412.19 cm^{-1} peak region), OH-groups (3200-3600 cm^{-1} peak region) and phosphonic moiety. On comparing the original herbicide spectral with those interacted with activated carbon, the functional groups common to both had different peaks information (denoting different peak heights, intensities and types of vibrations). This is an indication that there could be possibilities of either partial adsorption as observed from band shift, band distortion and not necessarily a band disappearance as applicable to complete or total adsorption. The role played by solvent action was also discussed.

Keywords: Glyphosate, Herbicide, Adsorption, Activated Carbon, FTIR, GCMS

INTRODUCTION

Among the different pollutants of aquatic ecosystem include herbicides, especially organo-chlorine herbicide like atrazine and organo-phosphorus pesticides such as glyphosate. They are considered as pollutants of high priority because they are harmful to aquatic lives even at $\mu\text{g/L}$ levels. These herbicides or pesticides consist of numerous groups of chemical structure thereby giving a wide range of physiochemical characteristics (Agdi et al., 2000). Although chemical herbicides have greatly improved yields in agriculture and forestry (Hanson and Fernandez, 2003) their non-target impacts have caused considerable concern (Albers et al., 2009).

Glyphosate herbicides are the mostly commonly used herbicides in the U.S. and the world. In agriculture they are widely used with genetically-modified glyphosate-tolerant crops, but they are also widely used in yards, gardens, and other nonagricultural areas. Glyphosate-based herbicides are among the most widely used broad-spectrum herbicides in the world because they are highly efficacious, cost effective, practically non-toxic, and degrade readily in the environment. Glyphosate is soluble in water, and tends to bind tightly to sediment, suspended particulates, organic matter and soil, becoming essentially unavailable to plants or other aquatic organisms. Glyphosate does not bio accumulate in terrestrial or aquatic animals (Giesy et al., 2000, Williams et al., 2000). Herbicidal effects are therefore

limited to foliar contact, cut stump or stem injected applications on plants. Glyphosate rapidly dissipates from surface waters, and soil micro-flora quickly biodegrade glyphosate into AMPA and CO_2 (Gardner and Grue, 1996).

Activated Carbon (AC) is the common term used for a group of absorbing substances of crystalline form, having a large internal pore structures that make the carbon more absorbent (Itodo et al., 2011). These properties are obtained when a char is subjected to controlled gasification by oxidizing gases, or when a raw material impregnated with dehydrating agents is subjected to carbonization (Itodo et al., 2011).

Technological methods of removing pesticides from water include:- oxygenation with strong oxidants, i.e. with chlorine, ozone, hydrogen peroxide, potassium permanganate,- photochemical exposure to UV rays,- biochemical decomposition by means of bio filter, activated sludge and soil microorganisms,- mechanical, i.e. filtration, rotation, sedimentation,- coagulation with aluminium sulphate, iron sulphate, iron chloride, Adsorption on natural and artificial materials, i.e. peat, clays, bentonite, humus, ionite, active carbons, zeolite, and others. Adsorption is a process in which a soluble chemical (adsorbate) is removed from a liquid by contact with a solid surface (adsorbent). It is used industrially for the separation and waste treatment of industrial products. Adsorption is actually a mechanism in which the forces of interaction between the surface atoms and the adsorbate molecules are similar to van

der waals forces of attraction that exists between all adjacent molecules (LaGrega et al.,1994)

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be the ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction (Hanson and Fernandez, 2003) Research carried out by, Itodo et al.,(2009), adopted gas chromatography for the prediction of equilibrium phase atrazine using homemade activated carbon. It was reported that Gas Chromatography- Mass spectrophotometer (GC/MS) can quantitatively estimate the amount of herbicide adsorbed.

Another research by Martinez and Brown, (1991) found the possibilities of oral and pulmonary toxicity of the surfactant used in Roundup herbicide and the use of activated carbon may be possible outlet.

In a research by Feng et al., (1990) the fate of Glyphosate in a Canadian Forest Watershed was studied.

Glyphosate: (N-(phosphonomethyl)glycine) is a broad-spectrum systemic herbicide used to kill weeds, especially annual broadleaf weeds and grasses known to compete with crops grown widely across the Midwest of the United States. Glyphosate is the most used herbicide in the USA (U.S. EPA., 1990). While glyphosate has been associated with deformities in a host of laboratory animals, its impact on humans remains unclear (Graves, 2011).

Chemistry of Glyphosate Herbicides: Glyphosate (N-[phosphonomethyl]glycine) is a weak organic acid comprising a glycine moiety and a phosphonomethyl moiety. Glyphosate prevents the synthesis of aromatic amino acids in plants and some microorganisms by inhibiting the enzyme 5-enolpyruvyl shikimate-3-P synthetase (Torstensson, 1985). There are many different commercial formulations of glyphosate herbicide that, in addition to the active ingredient, contain a number of additives to increase efficacy. Most of these additives are inert and their identities are protected as trade secrets. Of these additives, the available information shows that certain surfactants pose the greatest ecotoxicological risk. Surfactants reduce surface tension and increase wetting of hydrophobic plant cuticles, increasing penetration of glyphosate into plant tissues. A common surfactant in

glyphosate herbicides is polyoxyethyleneamine (also called polyoxyethyleneamine, POEA). In addition to POEA, several other surfactants are used in commercial formulations of glyphosate (Thompson, 1989). Although there is some understanding of the toxic effects of POEA, the ecotoxicological properties of the other surfactants are virtually unknown (Mann and Bidwell, 1999).

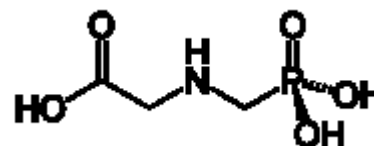


Fig. 1 Chemical Structure of Glyphosate. Herbicide details:

IUPAC name: N-(phosphonomethyl)glycine

Other names: 2-[(phosphonomethyl)amino]acetic acid

Herbicide Basics Chemical formula: N-(phosphonomethyl) glycine

Target Species: most annual and perennial plants

Forms: salts

Mode of Action: amino acid synthesis inhibitor

Water Solubility: 900,000 ppm

Adsorption potential: high

Primary degradation mechanism: slow microbial metabolism

Glyphosate is an aminophosphonic analogue of the natural amino acid glycine, and the name is a contraction of gly(cine) phos(phon)ate. The molecule has several dissociable hydrogens, especially the first hydrogen of the phosphate group. The molecule tends to exist as a zwitterion where a phosphonic hydrogen dissociates and joins the amine group. Glyphosate is soluble in water to 12 g/L at room temperature (U.S. EPA, 1990).

Justification of this research: Beside the conversion of waste to useful resources in adsorbent generation, The toxicity of glyphosate herbicides have been conducted on rodents, dogs, rabbits, birds, fish, aquatic invertebrates and aquatic vegetation. These tests showed that glyphosate, while highly toxic to plants, is also toxic to some animals (Williams et al., 2000) However, Laboratory toxicology studies suggest other ingredients combined with glyphosate may have greater toxicity than glyphosate alone. For example, a study comparing glyphosate and Roundup found Roundup had a greater effect on aromatase than glyphosate alone (Richard et al., 2005). Another study has shown Roundup formulations and metabolic products cause the death of human embryonic, placental, and umbilical cells in vitro, even at low concentrations. The health criteria of glyphosate have been the concern of world Health Organization (WHO, 1994). A review of the eco toxicological data on Roundup shows there are at least 58 studies of the effects of Roundup itself on a range of organisms (Giesy et al., 2000). More recent research suggests glyphosate induces a variety of functional

abnormalities in fetuses and pregnant rats (Daruich et al., 2001). Also in recent mammalian research, glyphosate has been found to interfere with an enzyme involved testosterone production in mouse cell culture (Walsh et al., 2000) and to interfere with an estrogen biosynthesis enzyme in cultures of human placental cells (Richard et al., 2005). In vitro studies have shown glyphosate affects progesterone production in mammalian cells and can increase the mortality of placental cells (Richard et al., 2005).

It was also established that adsorption prevents glyphosate from being mobile in the environment except when the soil particles themselves are washed (Rueppel et al., 1977).

The aim of this present study is to generate activated carbon from local raw materials (Cocos nucifera or coconut shells), the adoption of instrumental techniques (FTIR and GCMS) for the qualitative investigation of glyphosate adsorption from liquid phases in consideration of solvent interplay. This research, being the first phase was expected to be a sure guide towards a further stage (Adsorption of certain functional groups and their quantification).

MATERIALS AND METHODS

Commercial Glyphosate, Presumably N-(phosphonomethyl) glycine with 360g glyphosate specification and with the trade name, Roundup Herbicide was purchased from a retailer's stand of the Agro-Chemical wing of Aliero Central Market, Kebbi State, Nigeria. Chloroform (CHCl₃) and Distilled water were used as solvents in a mixtures at different ratios i.e. 1:1, 3:1 and 1:3 for experiment G1, G2 and G3 respectively. Other materials used in this research include derived activated carbon using the one step activation scheme. Major analytical instruments include FTIR, GCMS (a model GCMS QP2010 plus Shimadzu, Japan).

Stock solution

0.028cm³ of the herbicide (Glyphosate) was introduced gently into a 100cm³ volumetric flask and separately diluted with each solvent mixture to the mark respectively. i.e. mixtures of ratios 1:1, 3:1 and 1:3.

Batch Adsorption Test

10cm³ of the stock solution of each mixture was carefully pipetted into each 100cm³ volumetric flask and dilute to the mark with distil water which makes the working solution. And 10cm³ of each sample mixture of the working standard i.e 1:1, 3:1 and 1:3 was pipette into each 250cm³ conical flasks and 2g of the commercial activated charcoal was interacted with the solution in the conical flask respectively and allowed to stand for 2hours contact time. The mixtures were filtered in the air tight sample holder and the filtrate was kept in the sample holder for analysis (Agdi et al., 2000). The research finds bases from an initial qualitative study on FTIR spectral characteristics of atrazine sorption described elsewhere by Itodo et al.(2009).FTIR analysis was run on the filtrate sample

in the sample holders and the original glyphosate was analyzed using Gas chromatography coupled with a mass spectrophotometer detector (GCMS).

Choice of equipment

Choice herbicide is a multicomponent mixture containing glyphosate (Analyte) and other moieties, which are very similar to glyphosate.

More so, the GC column has a very high efficiency which was claimed to be in excess of 400,000 theoretical plates. The column is about 100m long, a very dispersive type of stationary phase retaining the solute approximately in order of increasing boiling point. Helium carrier gas was selected because it can realize high efficiencies with reasonable analysis time.

GCMS Conditioning

The column was held at 600C in injection volume of 1μL and then programmed to 2500C. it was set at a start m/z of 40 and end m/z of 420. The detector (mass spectrophotometer) was held at 2500C above the maximum column temperature. The sample size was 1μL, which was split 100-1 onto the column and so the total charge on the column was about 1. Helium was used as the carrier gas at a linear velocity of 46.3 cm/sec and pressure of 100.2 kPa. Ionization mode is Electron Ionization (EI) at a voltage of 70eV. In this analysis, amplification and resolution for test herbicide was achieved by adjusting the threshold to 6000. Thus worse interference and solvent peaks were screened out leaving majorly the deflection of target compound (glyphosate) as it was made pronounced on the chromatogram. Baseline disturbance was linked to either hydrocarbon impurities. Impure carrier gas can also cause baseline instability. It can be corrected by changing the purifier when pressure drops reaches 10-15 pSi (0.7-1.1 bar) routinely monitoring the pressure. Sorption efficiency of an adsorption process is defined based on the fractions of extracted and unextracted solutes.

Physicochemical parameters: The characterization experiment includes the determination of pH, Conductivity, porosity and density of the CAC. Some of these entailed the preparation and standardization of certain solutions (Aziza, 2008; Igwe and Abia, 2003)

For pH: 1g of CAC was weighed and dissolved in 20cm³ of deionized water, this was warmed and allowed to cool then dipped the pH electrode into the solution and the value was read from the meter until a desirable pH were reached between 6-8 (Aziza, 2008; Igwe and Abia, 2003).

For Conductivity: 1g of CAC was weighed and dissolved in 20cm³ of deionized water, it was warmed and the conductivity electrode was dipped and the readings were taken from the meter (Aziza, 2008; Igwe and Abia, 2003).

For Bulk Density: A 10cm³ Cylinder was filled to a given volume with <0.5 commercial activated carbon,

it was compacted by tapping on the bench for at least 1-2 minutes till a volume was reached, v (cm^3). The weighed in g was then recorded. The bulk Density was calculated as (Ahmedna et al, 2000).

$$\text{Blk.density}(\text{g} / \text{cm}^3) = \frac{\text{wt.adsorbent}(\text{g})}{\text{vol.adsorbent}(\text{cm}^3)}$$

RESULTS AND DISCUSSIONS

Functional Group Identification (Qualitative Analysis)

The research carried out on the sorption of glyphosate onto activated carbon on the solvent mixtures with the glyphosate herbicide were presented as FTIR spectral (Figures 1- 3) which were summarized as Table 1.

Table 1

FTIR Interpretation for most probable peaks on the FTIR of the samples G1-G3

Experiment	Characteristic band peaks (cm^{-1})	Functional Group	Corrected Intensity	Corrected Area	Type of Vibration	Intensity
G1	3429.55	O-H	54.544	179.884	Stretch	Strong, Broad
G2	1643.41	C=O	37.830	22.297	Stretch	Strong
G3	1642.44	C=O	20.523	12.487	Stretch	Strong

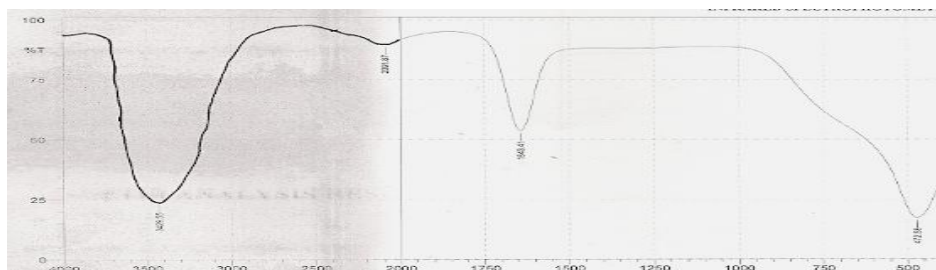


Fig. 1 Experiment G1-FTIR spectrum of Equilibrium phase Herbicide after Adsorption from 1:1 (Chloroform : Water) solution onto Commercial Activated Carbon.

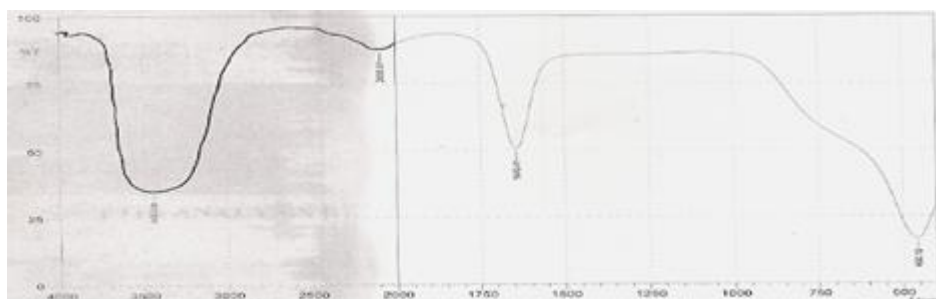


Fig. 2 Experiment G2 FTIR spectrum of Equilibrium phase Herbicide after Adsorption from 3:1 (Chloroform: water) solution onto Commercial Activated Carbon.

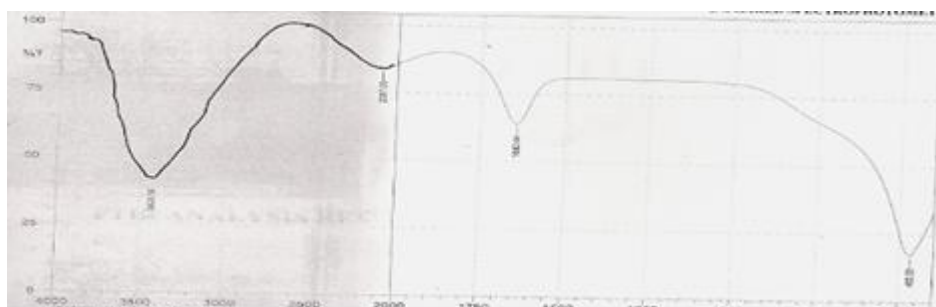


Fig. 3 Experiment G3- FTIR spectrum of Equilibrium phase Herbicide after Adsorption from 1:3 (Chloroform: Water) solution onto Commercial Activated Carbon.

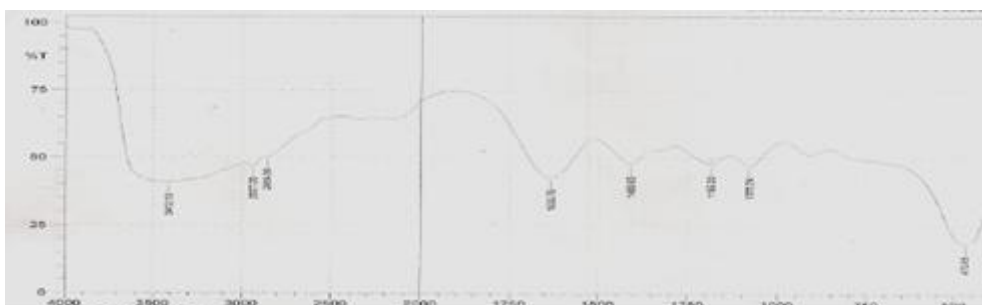


Fig. 4 FTIR spectral for the original and un-interacted Glyphosate (Herbicide)

The equilibrium phase herbicide and their functional groups were qualitatively analyzed after adsorption onto activated carbon. The results were compared to that of the original herbicide. The spectrums of the un interacted herbicide showed that the glyphosate is a multicomponent herbicide with several functional groups.

The earlier FTIR spectra above showed above (Fig. 1-3) indicated that the peak, 3429.55 is common to the three equilibrium phase samples, G1-G3. This bands has IR frequency that falls within the range 3200-3600 cm^{-1} and 3300-3500 cm^{-1} and representing the

characteristic IR absorption Frequency of organic functional groups. The range, 3200-3600 cm^{-1} has O-H (hydroxyl) functional group, Hydrogen bonded vibration of broad intensity while the range from 3300-3500 cm^{-1} is for N-H (Amine) functional group. A comparison with the suspected compounds from the GCMS results in Line 3, HIT 1 showed that the range 3200-3600 cm^{-1} is the most probable functional group of the band peak because there is presence of compounds with (O-H) hydroxyl group. This was presented as figure 5.

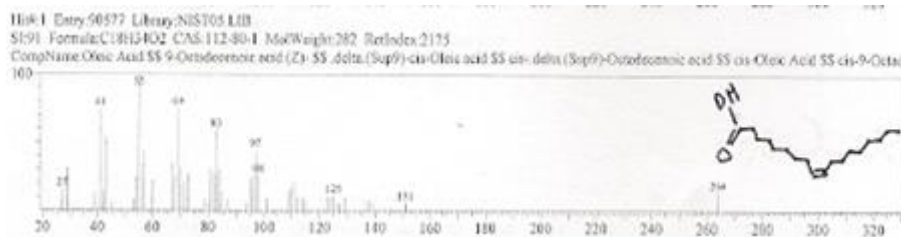


Fig. 5 GCMS Chromatogram showing a Line 3, HIT 1 compound as Oleic Acid of 91% similarity index with O-H group in glyphosate herbicide.

Other suspected compounds in the herbicide formulation where presented on the chromatograms as Octadecanoic Acid (Figure 6), 3,4-Oxazolidinedicarboxylic acid (Figure 7), Octadecanoic Acid (Figure 8) on hosts of others.

The peak band in the 1640-1690 cm^{-1} range which displayed a C=O (Carbonyl) functional group with

strong intensity and a stretch type of vibration was however found that the actual functional group for this peak is 1643.41 as confirmed from GCMS result in fig 6 and 7 to be linked to hit compounds like

Octadecanoic Acid with 90% similarity index (Fig. 6) and 3,4-Oxazolidinedicarboxylic acid with 66% similarity index (Fig. 7).

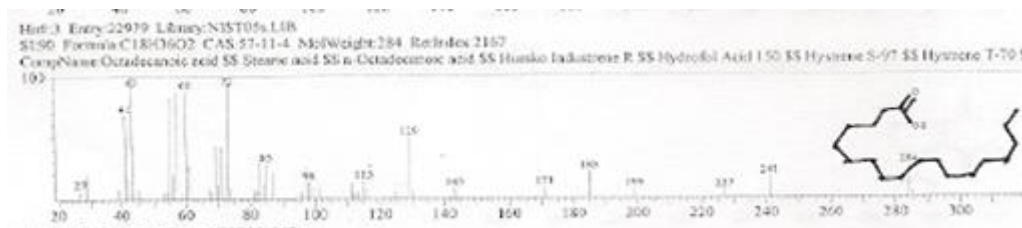


Fig. 6 GCMS spectra showing the suspected compound Octadecanoic Acid with 90% similarity index in glyphosate herbicide.

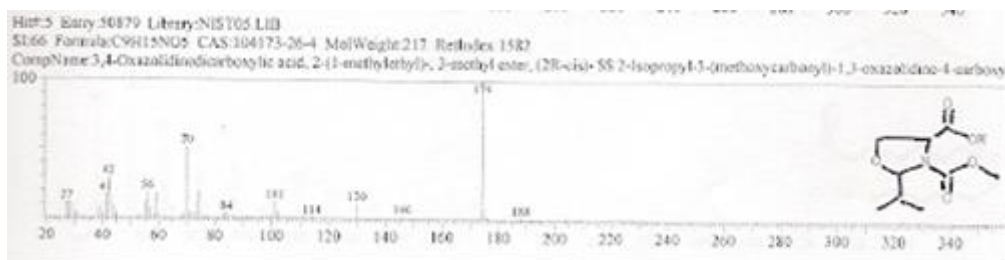


Fig. 7 GCMS spectra showing the suspected compound 3,4-Oxazolidinedicarboxylic acid with 66% similarity index in glyphosate herbicide.

Adsorption Performance Assessment

The peak 1643.41 at G1, 1643.41 at G2 and 1642.44 at G3 which fell within the range of those assigned to C=O functional groups evidently remain un-adsorbed onto the activated carbon irrespective of the solvent action. This was deduced from the fact that the same peak is present in the FTIR spectrum of the original untreated herbicide. Other un-adsorbed groups are those of the OH, N-H (Amine) etc.

Other indications of adsorption is the fact that comparing the original herbicide spectral (Fig. 4) with those interacted with activated carbon (Figures 1-3), the functional groups common to all had different peaks information (Different peak heights, intensities and types of vibrations). This is an indication that there could be possibilities of either partial adsorption which causes band shift, band distortion and not necessarily a band disappearance as applicable to complete or total adsorption. For example, the peak 3412.19 for the original herbicide is broad while that of the sample

solutions are sharp, thus there is band shift or distortion due to partial adsorption.

Also considering and comparing the Finger print region which ranges from 500cm^{-1} to 1500cm^{-1} of the original sample, it shows that, the activated carbon used has absorb the probable peaks in the sample mixtures G1-G3 of the finger print region whose bands mostly depicts C=C characterized alkene. Other adsorbed peaks in this region include those of which ranges from $500\text{-}1500\text{cm}^{-1}$.

More so, the peak bands 2937.68 and 2859.56 found in the FTIR of the original sample were absorbed by the activated carbon because they were completely absent in the tests samples for residual herbicides. Reoccurring peaks of 3412.19 and 1633.76 were unabsorbed because they appear in the analytical sample mixtures. And their functional groups are probably as confirmed by the GCMS results which are the C=O group and the O-H group from figure 3.8 to 3.9.

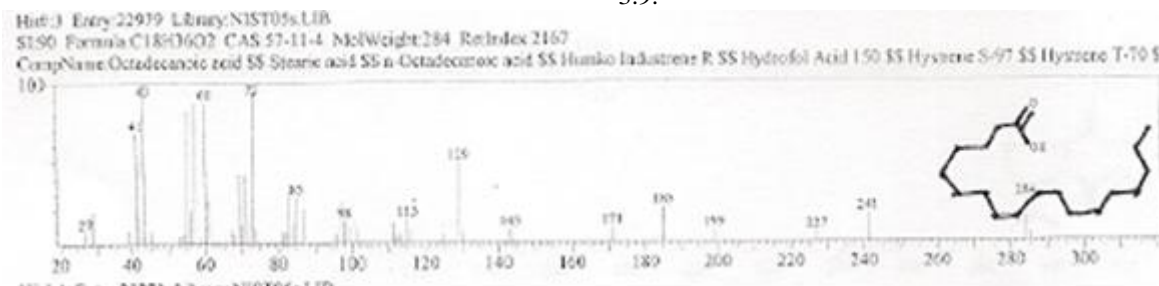


Fig. 8 GCMS spectra showing the suspected compound Octadecanoic Acid with 90% similarity index.

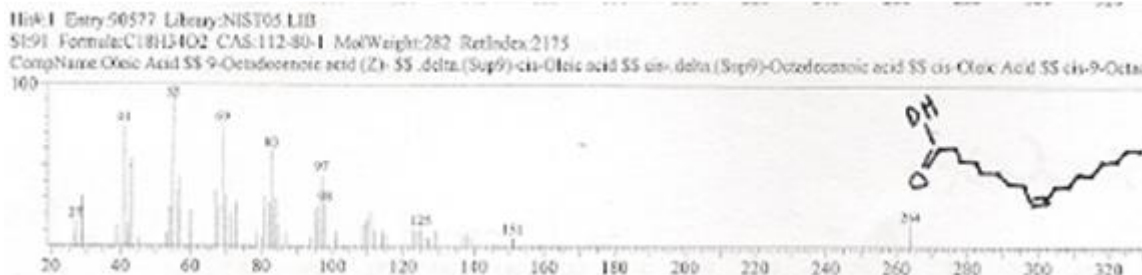


Fig. 9 GCMS spectra showing the suspected compound Oleic Acid with 91% similarity index

Solvation Role

The role played by solvent was investigated. Solvent action cannot be overlooked because it affects the intensity of adsorption. For sample G1, the corrected intensity for the peak 1643.41 is 37.83, that of G2 is 39.39 while for G3 stands as 20.523. This confirms the role that the extent of adsorption greatly depends on the chemical environment of the adsorbate under consideration. This present analysis revealed that equilibrium phase or un-adsorbed glyphosate is higher in samples of G1 and G2 where we are having higher intensities due to the high quantity of organic solvent, (chloroform) than water. Hence, interaction activated carbon with glyphosate herbicide in which organic solvent is having high concentration in the solvent mixture gave poor adsorption compared to when there is high water in the mixture ratio as exemplified in 1:3 (Chloroform : Water) for interacting activated carbon.

In this comparative study, functional groups with least intensities are indication of better adsorption than those of high intensities. This present studies strongly

agreed with the facts that the solvent action of glyphosate and the herbicide affinity for sorption sites is higher in water than in organic solvent. This also signified that if only water was used as solvent to interact with the herbicide, the C=O would have totally disappeared and the activated carbon might have absorbed the functional group present to a better extents.

GCMS Prediction of the Multicomponent Formulation/Composition of the glyphosate Herbicide

The general chromatogram from the original glyphosate herbicide presented six lines (Line 1-6). These six lines signifies six major compounds with each major compounds having several suspected compounds (Hits) of variable similarity represented as similarity indices (% SI).



Fig. 10 GCMS Chromatogram of un-interacted glyphosate with six different lines

Tables 2 – 8 represents the several suspected compounds (Hits) for each of the compound line detected in the chromatogram of Figure 10

Table 2

List of Compounds in Line 1

Line/Compound	HITS	SI	Mol. Formula	Mol. weight	Name of Compounds
1	1	94	C ₁₆ H ₃₂ O ₂	256	Hexadecanoic Acid
	2	90	C ₁₆ H ₃₂ O ₂	256	Hexadecanoic Acid
	3	90	C ₁₈ H ₃₆ O ₂	284	Octadecanoic Acid
	4	90	C ₁₅ H ₃₀ O ₂	242	Pentadecanoic Acid
	5	89	C ₂₀ H ₄₀ O ₂	312	Eicosanoic Acid

SI- Similarity index (Level of resemblance to suspected compounds)

Table 3

List of Compounds in Line 2

Line/Compound	HITS	SI	Mol. Formula	Mol. weight	Name of Compounds
2	1	76	C ₇ H ₁₅ NO ₄ Si	205	1-Methoxy-2,8,9,-trioxa-5-aza-1-silabicyclo(3.3.3)undecane
	2	68	C ₁₂ H ₃₁ NO ₂ Si ₂	277	N,N-bis(2- Trimethylsiloxyethyl)ethanamine
	3	68	C ₉ H ₁₅ NO ₅	217	3,4-Oxazolidinedicarboxylic Acid
	4	66	C ₈ H ₁₇ NO ₃ Si	203	1-Ethyl-2,8,9-Trioxa-5-aza-1-silabicyclo(3.3.3)undecane
	5	66	C ₈ H ₁₇ NO ₃ Si	203	1-Ethyl-2,8,9-Trioxa-5-aza-1-silabicyclo(3.3.3)undecane

SI- Similarity index (Level of resemblance to suspected compounds)

Table 4

List of Compounds in Line 3

Line/Compound	HITS	SI	Mol. Formula	Mol. weight	Name of Compounds
3	1	91	C ₁₈ H ₃₄ O ₂	282	Oleic Acid
	2	90	C ₁₈ H ₃₄ O	266	Z-13-Octadecenal
	3	89	C ₁₆ H ₃₀ O	238	Z-9-Hexadecenal
	4	89	C ₂₂ H ₄₂ O ₂	338	Cis-13-Docosenoic Acid
	5	89	C ₁₈ H ₃₄ O ₂	282	6-Octadecenoic Acid.

Table 5

List of Compounds in Line 4

Line/Compound	HITS	SI	Mol. Formula	Mol. weight	Name of Compounds
4	1	69	C ₁₂ H ₃₁ NO ₂ Si ₂	277	N,N-bis(2-Trimethylsiloxyethyl) ethanamine.
	2	68	C ₇ H ₁₅ NO ₄ Si	205	1-Methoxysilatrane
	3	67	C ₇ H ₁₄ N ₂ OS	174	4,6-Dimethyl-1-oxa-4,6-diazacyclooctane-5-thione
	4	67	C ₈ H ₁₇ NO ₃ Si	203	1-Ethylsilatrane
	5	66	C ₉ H ₁₅ NO ₅	217	3,4-Oxazolidinedicarboxylic acid.

SI- Similarity index (Level of resemblance to suspected compounds)

Table 6

List of Compounds in Line 5

Line/Compound	HITS	SI	Mol. Formula	Mol. weight	Name of Compounds
5	1	84	C ₁₈ H ₃₁ ClO	298	9,12-Octadecadienoyl chloride
	2	83	C ₁₆ H ₃₀ O ₂	254	1,2-15,16-Diepoxyhexadecane
	3	83	C ₅₇ H ₁₀₄ O ₆	884	9-Octadecenoic acid
	4	82	C ₁₈ H ₃₄ O	266	Z,E-2,3-Octadecadien-1-ol
	5	82	C ₁₄ H ₂₆ O	210	7-Tetradecenal

SI- Similarity index (Level of resemblance to suspected compounds)

Table 7

List of Compounds in Line 6

Line/Compound	HITS	SI	Mol. Formula	Mol. weight	Name of Compounds
6	1	68	C ₉ H ₁₅ NO ₅	217	3,4-Oxazolidinedicarboxylic acid
	2	68	C ₇ H ₁₅ NO ₄ Si	205	1-Methoxy-2,8,9-trioxa-5-aza-1-silabicyclo(3.3.3)undecane
	3	67	C ₈ H ₁₇ NO ₃ Si	203	1-Ethyl-2,8,9-trioxa-5-aza-1-silabicyclo(3.3.3)undecane
	4	66	C ₁₂ H ₃₁ NO ₂ Si ₂	277	N,N-bis (2-Trimethylsiloxyethyl) ethanamine
	5	65	C ₁₃ H ₂₀ N ₂	204	2-(4-Phenyl-piperidine-1-yl)-ethylamine

SI- Similarity index (Level of resemblance to suspected compounds)

Table 8

GCMS Specification for most suspected Compounds in Glyphosate.

LINES	S.I (%)	Mol. Formula	Mol. Weight	Names of Compounds
1	94	C ₁₆ H ₃₂ O ₂	256	Hexadecanoic Acid
2	68	C ₉ H ₁₅ NO ₅	217	3,4-Oxazolidinedicarboxylic Acid
3	91	C ₁₈ H ₃₄ O ₂	282	Oleic Acid
4	69	C ₁₂ H ₃₁ NO ₂ Si ₂	277	N,N-bis(2-Trimethylsiloxyethyl)ethanamine.
5	84	C ₁₈ H ₃₁ ClO	298	9,12-Octadecadienoyl chloride
6	68	C ₉ H ₁₅ NO ₅	217	3,4-Oxazolidinedicarboxylic acid

SI- Similarity index (Level of resemblance to suspected compounds)

CONCLUSION

Highlights of this research revealed that the need for FTIR and GCMS analyses are critical in the qualitative study of herbicide sorption onto derived, received or formulated adsorbent prior to quantification study. Results obtained for the Herbicide (Glyphosate)

depicts that it is a multicomponent sample, has partial affinity for activated carbon and that this attractive power can be enhanced with the appropriate solvent, being water.

APPENDIX

Table 9

FTIR information of the original sample (Glyphosate) (control).

S/N	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	470.65	18.770	19.804	856.42	399.28	194.404	32.843
2	1078.24	47.173	5.719	1131.29	980.84	44.022	3.239
3	1185.30	47.806	4.521	1285.60	1132.25	45.644	3.099
4	1409.05	47.746	6.882	1509.35	1347.32	46.482	4.526
5	1633.76	42.789	19.988	1906.70	1510.31	96.236	24.018
6	2859.56	50.290	0.069	2861.49	2441.96	96.636	0.112
7	2937.68	46.991	1.697	2980.12	2862.46	37.167	0.779
8	3412.19	40.833	30.759	3883.80	2981.08	264.896	116.004

Table 10

FTIR Information of Equilibrium Phase Glyphosate after sorption onto Commercial Activated Carbon.
(Adsorbent:Adsorbate solution =1g:5ml, Chloroform: Water = 1:1).

S/N	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	472.58	17.390	20.886	1082.10	399.28	183.301	27.022
2	1643.41	53.632	37.830	1856.55	1448.59	37.935	22.297
3	2091.87	89.640	5.0480	2320.44	1856.55	16.146	5.162
4	3429.55	23.970	71.298	3839.44	2589.52	287.231	263.783

Table 11

FTIR Information of Equilibrium Phase Glyphosate after sorption onto Commercial Activated Carbon.
(Adsorbent:Adsorbate solution =1g:5ml, Chloroform :Water = 3:1).

S/N	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	456.18	16.457	17.188	1095.60	399.28	193.471	22.631
2	1643.41	50.594	39.390	1856.55	1388.79	48.055	25.703
3	2090.91	87.654	6.762	2592.41	1857.51	25.772	9.051
4	3443.05	35.275	59.556	3839.44	2593.38	258.507	231.913

Table 12

FTIR Information of Equilibrium Phase Glyphosate after sorption onto Commercial Activated Carbon.
(Adsorbent:Adsorbate solution =1g:5ml , Chloroform :Water = 1:3).

S/N	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	465.82	17.254	20.092	1168.90	399.28	185.109	22.363
2	1642.44	64.048	20.523	1858.48	1513.21	35.776	12.487
3	2087.05	83.667	0.062	2088.98	1876.80	13.134	0.230
4	3428.58	42.377	54.544	3869.33	2626.17	193.074	179.884

Table 13

FTIR Information on Commercial Activated Carbon.

S/N	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	577.70	31.4097	36.0632	804.34	433.03	95.0773	33.1895
2	1037.74	11.2438	53.1962	1297.17	888.25	175.6768	99.3659
3	1441.84	42.4418	18.2671	1569.14	1298.14	76.7155	18.3495
4	1630.87	51.6459	9.8635	1857.51	1570.11	46.2338	0.0515
5	2012.79	74.8463	8.6027	2070.65	1857.51	17.8210	2.4088
6	3429.55	31.6647	32.7780	3728.53	2248.11	412.2857	176.6807

Table 14

FTIR Information on Chloroform (Solvent).

S/N	Peak	Intensity	Corr. Intensity	Base (H)	Base (L)	Area	Corr. Area
1	463.90	10.916	4.839	800.49	448.46	84.699	1.593
2	1285.6	92.48	2.059	1331.89	1224.84	3.124	0.535
3	1371.43	92.512	0.143	1374.33	1331.89	1.295	0.035
4	1458.23	91.271	0.105	1508.38	1457.27	1.441	0.010
5	1699.34	90.775	0.185	1701.27	1654.01	1.574	0.014
6	2349.38	94.744	1.300	2414.96	2263.54	3.064	0.421
7	2931.90	79.833	14.665	3170.11	2746.73	19.194	8.796

REFERENCES

- Agdi K, Bouaid A, Martin E, Fernandez H, Azmani A Camara, Removal of atrazine from environmental water by diatomaceous earth remediation method. *J. Environ. Monitor*, 2, 420-423, 2000.
- Ahmedna M, Marshal W, and Rao M, Production of Granular activated carbon from selected Agric bye products. *Bioresources Technology*; 71(2): 113-123, 2000.
- Albers BG, Hansen P, Jacobsen O, The influence of organic matter on sorption and fate of glyphosate in soil comparing different soils and humic substances, *Environmental pollution*, 157 (10), 2865–2870, 2009.
- Aziza A, Odiakosa G, Nwajei, V. Orodu V, Modification and characterization of activated carbon derived from Bumper sawdust and disk sawdust to remove lead (II) and cadmium (II) effluent water. *CSN Conference proceeding. Chemical Society of Nigeria, Deltachem*, pp, 235-243, 2008.
- Daruich J, Zirulnik F, Gimenez MS, Effect of the herbicide glyphosate on enzymatic activity in pregnant rats and their fetuses, *Environmental Research* 85 (3), 226–31, 2001.
- Hanson KG, Fernandez MR, In-vitro growth of fusarium head blight as affected by glyphosate-based herbicides. *Canadian Journal of Plant Pathology*, 25,120, 2003.
- Feng, JC, Thompson DG, Reynolds PE, Fate of Glyphosate in a Canadian Forest Watershed. 1. Aquatic Residues and Off Target Deposit Assessment. *J. Agric. Food Chem.* 38, 1110-111. 1990.
- Gardner S, Grue C, Effects of Rodeo and Garlon 3A on Nontarget Wetland Species In Central Washington. *Environ Toxicol Chem, Bol* 15, (4), 441-451, 1996.
- Giesy JP, Dobson S, Solomon KR, Ecotoxicological Risk Assessment for Roundup Herbicide. *Rev Env. Contam Toxicol*, 167,35-120, 2000.
- Graves L, Roundup Birth Defects: Regulators Knew World's Best-Selling Herbicide Causes Problems, *New Report Finds, Huffington Post*, 9, 2011.
- Hanson KG, Fernandez MR, In-vitro growth of fusarium head blight as affected by glyphosate-based herbicides. *Canadian Journal of Plant Pathology*,25,120, 2003.
- Igwe JC, Abia AA, Maize cob and husk as adsorbent for removal Cd, Pb and Zn ions from waste water. *The physical science*, 2, 83-94, 2003.
- Itodo AU, Abdulrahman FW, Hassan LG., Atiku FA, Itodo HU, GCMS Prediction of Organochlorine Herbicide Sorption Rate: A Batch Kinetic Studies, *Trends in Applied Sciences Research*, 6(8), 451-462, 2011.
- Itodo AU, Abdulrahman FW, Hassan LG, Maigandi SA, Itodo HU, Gas Chromatographic Prediction of Equilibrium Phase Atrazine after Sorption onto Derived Activated Carbon, *International Journal of Poultry Science*, 8, 1174-1182, 2009.
- LaGrega M, Buckingham P, Evans J, Environmental Resources Management Group, Hazardous Waste Management, McGraw-Hill Inc., New York, NY, 1994.
- Mann RM, Bidwell JR. The toxicity of glyphosate and several glyphosate formulations to four species of Southwestern Australian Frogs. *Arch Environ contam. Toxicol.* 36, 193-199, 1999: In
- Mann, RM, Toxicological impact of agricultural surfactants on Australian amphibians. Curtin University of Technology, Sydney, Australia. Available at <http://adt.curtin.edu.au/theses/available/adt-WCU20031202.161329/>, 2000.
- Martinez TT, Brown K, Oral and pulmonary toxicity of the surfactant used in Roundup herbicide. *Proc. West. Pharmacol. Soc*, 34,43-46, 1991.
- Richard S, Moslemi S, Sipahutar H, Benachour N, and Seralini GE, Differential effects of glyphosate and Roundup on human placental cells and aromatase. *Environ. Health Perspect*, 113, 716–720, 2005.
- Rueppel ML, Brightwell BB, Schaefer J, and Marvel JT, Metabolism and degradation of glyphosate in soil and water. *J. Agric. Food Chem.* 25,517-528, 1977.
- Thompson J, Chronic effects of sub-lethal levels of dalapon, gluphosate and 2,4-D amine on the lymnaeid snails pseudo succineacolumella and Fossariacubensis, M.S thesis, southern University Library, Baton Rouge, L.A, 1989.
- Torstensson L, Behavior of glyphosate in soils and its degradation, *The Herbicide Glyphosate*, Chap, Swedish University of Agricultural Sciences, Upsala, Sweden, 9, 137-150, 1985.
- U.S. EPA, Pesticide Fact Handbook, Noyes Data Corporation, Park Ridge, New Jersey, 2, 301-312, . 1990.
- Walsh L P, McCormick C, Martin C, Stocco DM, Roundup inhibits steroidogenesis by disrupting steroidogenic acute regulatory (StAR) protein expression, *Environmental health perspectives Environmental Health Perspectives*, 108, 8, 769–776, 2000.
- Williams GM, Kroes R, Munro IC, Safety evaluation and risk assessment of the herbicide Roundup and its active ingredient, glyphosate for humans, *Regulatory Toxicol and Pharmacol.* 31,117–165, 2000.
- WHO, Glyphosate. *Environmental Health Criteria No. 159*. World Health Organization, Geneva, 1994.