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Soil lixiviation and slow release pattern of starch-nano sliver particles-encapsulated dichlorvosinsecticide formulation

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Abstract: *The mobility of dichlorvos from starch-silver nano slow release formulations (AgSRF) was studied in three different soils in Nigeria. Encapsulation of dichlorvos into starch silver matrix was achieved in situ via chemical reduction of $AgNO_3$ by glucose under direct heating. This slow release formulation of nanosilver (AgSRF), according to the UV/Vis spectra depicted a peak at 419 nm which has been reported to be the characteristic of the Surface Plasmon Resonance (SPR) of silver nanoparticles. The morphology is spherical and size range of 23 -35 nm and X-ray diffraction showed it is partly crystalline. Insecticide release in soil and water was in the order sandy-loam > sandy-clay-loam > clay-loam. This nanoformulation (AgSRF) was compared to technical and commercial grades of dichlorvos respectively. AgSRFmatrix revealed sustained release behaviour more than technical and commercial (EC). In the lixiviation studies, each treatment was analysed in a column (in a duplicate) packed with soil. The columns were leached with 50 -100ml of buffer (pH 6.5) medium for 10 - 14 days. The soils ranking in leach pattern of insecticide in soil was in the order sandy-loam (48.1%)> sandy-clay-loam (33.9%) > clay-loam (22.4%).The formulations technical and Emulsifiable concentrate had same leach behaviour. The AgSRF formulation showed greater retention of dichlorvos in the soil surface (53%) during desorption rinse compared to technical (21%) and Emulsifiable Concentrate (12%).*
Key words: *Insecticide, leaching, release, nanoparticle, Dichlorvos, soil*

I. Introduction

The economies of the third world countries is built on agriculture which recently has been experiencing major challenge in meeting population's food demands. Other issues includeshigh production costs due to the high cost of farm inputs like fertilizer and pesticides as well as an increasing risk of pests and diseases.Synthetic chemical pesticides (e.g. organophosphates) are widely used to combat crop loss and their indiscriminate usage is rarely checked in many countries. Their use is wasteful as only 0.1% of the chemicals used in crop protection reaches the target pest while the rest enters the environment and may cause hazards to non-target organisms, including humans(Roy et al, 2014). Dichlorvos, o-2,2-dichlorovinyl-o,o-dimethyl phosphate (DDVP; VOS) (Figure 1), that is extensively used in many countries mostly developing countries for controlling insect pests on agricultural, commercial, domestic, and industrial sites.It is expensive as it is imported in to Nigeria at high exchange rate (Tijani and Oshotimehin, 2007 and Omolehinet al, 2011).

Modification of mode of delivery to ensure environmental safety and that of the farmer has necessitated an alternative. Slow release formulations which allows the delivery of an active ingredient to a targeted surface over a period of time is known to give effective treatment, reduced side effects, prolonged efficacy, and enhanced safety and reliability (Roy et al, 2014). The use of nanomaterials for the controlled delivery of fertilizers and pesticides is nascent technology that has the potential to increase the efficiency of food production and decrease pollution (Wanyika, 2012). The active ingredients are dissolved, entrapped, encapsulated or attached to nanoparticles (1 to 100 nm). Starches have found application in the delivery of pesticides and other active ingredients (Szymońskaet al, 2009). It is also a vehicle to carry and stabilize silver nanoparticles (AgNPs) (Ihegwuagu et al, 2014). AgNPs has been reported to possess unique properties such as size, shape and even antimicrobial activities (Gao et al, 2011, Niraimathiet al, 2013). Many methods have been reported in developing silver nano-products including chemical reduction method (Ihegwuagu et al, 2014).

Development of nanospheres to improve the delivery of insecticides to plants and soil is nascent and more research in this area is needed since the environmental fate of pesticides is mainly regulated by their behaviour in soil where various physico- chemical and biological processes control their dissipation (Boehm et al. 2003, Bajeeret al, 2012).Extensive research has been done on pesticide in relation to its mobility and leaching potential in soils (Gunanandet al, 2006, Bajeeret al, 2012).Leaching in soil columns have been carried out (Bakouriet al., 2007, Arias-Este´vez,et al., 2007;Alisteret al., 2011, Bajeeret al. 2012 &Ebelinget al., 2013) and found that behaviours of most pesticides are generally influenced by the content of organic carbon in soil. Also, sorption is one of the most important processes affecting the leaching of pesticides through soil because it controls the amount of pesticide available for transport (Cao et al., 2008, Alisteret al., 2011 &Ebelinget al., 2013). Maquedaet al, (2008) suggested that the use of these novel controlled release formulations could minimize the risk of groundwater contamination while maintaining pest/weed control for a longer period. In this direction, the present investigation reports the insitu synthesis andleaching pattern cum aqueous release behaviour ofstarch-silver nanodichlorvos insecticide formulation in comparison with the technical and commercial (EC) formulationsin the soil.

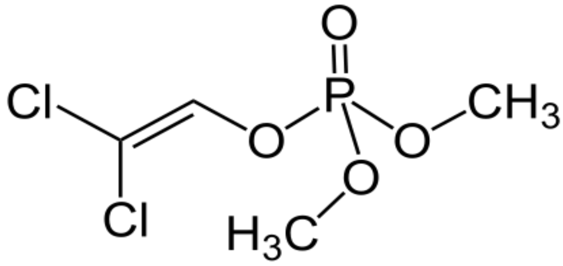

Figure1: molecular structure of dichlorvos, O-2,2-dichlorovinyl-O,O-dimethyl phosphate (DDVP)

II. Materials And Methods

2.1 Chemicals and material

Chemicals employed in this study were purchased and used without further purification. Silver nitrate ($AgNO_3$), 98%, Sigma Aldrich, Germany, Glucose, was purchased from Finlab Chemical Company, Abuja, Nigeria. Technical Dichlorvos (DDVP), 95% from AgroChina Company, Shanghai China (formula weight is 220.98g/mol, molecular formula of $C_4H_7Cl_2O_4P$. A commercial DichlorvosEmulsifiable Concentrate (EC) formulation (Delvap1000EC)) was purchased from Candel agrochemical in Nigeria. Native cassava starch powder was extracted from cassava tubers bought from Karmo Market, Abuja, Nigeria. All solutions were prepared using distilled water. Dichlorvos stock solution was prepared in acetone and other working solutions were prepared by diluting the stock solution.The native cassava starch was extracted and defatted according to reported methods with modification (Ihegwuagu et al, 2009).

2.2. Soil sampling

Three soil samples were collected from Abuja, the north central and Federal Capital City (FCT) of Nigeria. FCT is on latitude 9.08^{o}N and longitude 7.53^{o}E. Sampling sites were from two areas that are not exposed to farming activities to avoid interference from applied fertilizers and pesticides. Two soil samples were collected from the Gwarinpa Estate in the Abuja Municipal Area Council (AMAC). The first sample (brownish) was Gwarinpa 1, coded GWA and the secondGwarinpa 2 was coded LTE (this was reddish brown). The third soil sample (darker brown) was from Sheda (Gwagwalada area council, Abuja) and was coded SHD.

About 1kg soil sample was collected 15cm deep the earth from each site and colour and texture noted respectively. These were kept in appropriately labelled polythene bags in the laboratory, then air dried for 10 days the dried soil samples were sieved through 2.0mm after which they were gently pulverized with a porcelain mortar and pestle and kept in sealed plastic bags at room temperatureprior to analysis according to Nnamonu, (2011). The pH of soil was determined in both distilled water and 0.01M $CaCl_2$ employing properly calibrated pH meter (CRISO pH meter 25).The standard methods were used to determine physicochemical properties of the soil (OECD, 312, 2004), which are given in **Table 1**.

2.3 Synthesis of Nanosilver dichlorvos loaded Slow Release Formulations

Starch- silver nanoparticles-encapsulated dichlorvos was synthesized in-situ by direct physical gelation method during the chemical reduction of silver nitrate by glucose as described in section 3.3.1, according to Gao et al, (2011) and Saifudinet al, (2011). A complex of 0.06M $AgNO_3$ and 0.2M glucose solution in a flask containing 1% starch dispersion (in distilled water) and active ingredients (a.i) (0.0034M technical grades of dichlorvos) were stirred in a flask for 10mins and the complex was heated for 3 hours. The resultant hot complex was cooled and centrifuged at 11,000rpm for 20minutes using Eppendorf 5417R micro-Centrifuge.

Subsequently, the ST-AgNP-VOS nanoformulation was precipitated with addition of acetone (30ml), re-centrifuged at 6000rpm for 5minutes and sediment oven-dried at 40 ^{o}C for 24hours. The resulting nanocomposite was finely ground, kept in a sample bottle, and stored in a vacuum desiccator devoid of light for further use and characterization. A similar procedure was performed for the preparation of the control without the addition of $AgNO_3$ and glucose just the conventional DDVP.

2.4 Characterization Techniques

UV–Visible spectral analysis was used to confirm the synthesis of the silver nanoparticles loaded with dichlorvos. However, appearance of sharp plasmon resonance band around 400 nm confirm presence of the of mono dispersed AgNPs, UV-visible spectrophotometer Agilent, Model 8453 Chemstation software was used for spectral recording.High Resolution Transmission Electron Microscope (HR-TEM) coupled with EDX (FEI TECNAI 02)applied in the morphological characterization of the nanoinsecticide ST-AgNP-VOS.

2.5 Mobility (leaching) of technical and Commercialgrades (EC) of Dichlorvos insecticide

The technical and commercial grade insecticide was applied at the rate of 350 – 750ml/ha (according to Farmlinx and Sahito, et al., (2013).

In duplicate, leaching (tubes) columns (internal diameter 3cm, 15cm long were fitted with cotton wool at base). They were packed with untreated, air-dried and sieved soil (< 2 mm) up to 4g. To obtain uniform packing, the soil was added to the columns in small portions with a spatula and pressed with a plunger under simultaneous gentle column vibration until the top of the soil column did not sink in further. Uniform packing was required for obtaining reproducible results from leaching columns. The packed column was irrigated with 2ml distilled water poured slowly at intervals of 2 minutes to mimic rain, which drained off by gravity after equilibration. Then a spiked (overnight- dried 1g soil sample mixture of accurately measured insecticide in a glass vial), sample was added on top the column, 1g soil and a thin layer of glass wool placed over the packing. Then, 5ml ofleaching medium (buffer of pH 6.5) was poured in with a syringe and this was donein ten successive portions mimicking ten rain incidents and eachleachate collected in glass vials for insecticide analysis using the UV-Vis spectrophotometer (Lima et al, 2010, Nnamonu, 2011).

2.5.1 Desorption Study

In the desorption studies, 7 successive extractions of adsorbed insecticide on the moist leached soil (in duplicate), was carried out. The soil was re-suspended in buffer 6.5 solution and agitated for 24 hours. This was centrifuged at 4000rpm for 20 minutes and with the aid of UV-Vis spectrophotometer, the insecticides absorbance was determined and related to the calibration curve prepared. This rinse was carried out for 7days (Lima et al, 2010).

2.5.2 Aqueous release in soil(mobility of nano formulations)

The aqueous release study of the formulated nano-insecticides was carried out by same procedure for soil mobility experiment but the layer of active ingredient was replaced with an accurately weighed nano-insecticide atop the 4g soil-packed column (leaching tube). The release was studied for 14 days.

2.6 Statistical Analysis

In order to check the reproducibility of the results, all the experiments were performed at least two times (n =2) and the data summarized have been expressed as means ± s.d. whereas the error bars have been indicated in the data points in some of the Figures.

III. Results and Discussion

3.1 Soil properties

Table 1: Physical and Chemical Properties of the Soil Samples

Parameter	GWA	SHD	LTE
pH(in water)	8.38 ± 0.01	6.42± 0.01	5.07± 0.04
pH(0.01M $CaCl_2$)	7.23± 0.21	5.61± 0.01	4.25± 0.01
Sand (%)	77± 0.01	60± 0.001	53± 0.1
Silt (%)	14± 0.81	24± 0.35	15± 0.68
Clay (%)	9± 0.1	16± 0.05	32± 0.09
Moisture content (%)	0.1± 0.11	8± 0.24	1± 0.17
Total carbon (%)	13.4± 0.01	BD	6.7± 0.01
Organic matter (%)	0.23± 0.11	1.01± 0.01	0.12± 0.07
Cation Exchange Capacity(CEC):	5± 0.32	4.3± 0.17	4.7± 0.42
Texture	Sandy- loam	Sandy-clay-loam	Clay-loam

BD = below detection limit.

The physico- chemical properties of soil has been reported to significantly affect pesticide transport and the potential for groundwater contamination (Bajeer, et al., 2012). These properties include soil texture, organic matter, pH, cation exchange capacity, electrical conductance and moisture. Furthermore, the pesticide is more adsorbed to soil containing higher content of clay in its texture because the clay possesses a larger surface area [Bajeeret al., 2012). Meanwhile, GWA had the texture of sandy-loam; SHD had sandy-clay-loam, while LTE was classified clay-loam. The soil pH in water was higher than their pH in 0.01M $CaCl_2$. Where pH of soil sample GWA was 8.38 in water, it gave 7.23 in 0.01M $CaCl_2$, SHD had 6.42 in water and 5.61 in 0.01M $CaCl_2$.

Also, LTE soil had a pH of 5.07 in water and showed 4.25 in 0.01M $CaCl_2$.The soil LTE was most acidic while the most alkaline was GWA. The order of acidity was;LTE>SHD>GWA while alkalinity like the Cation Exchange Capacity had the same order; GWA>SHD>LTE. The organic matter followed the order SHD>GWA>LTE. The total carbon content was highest in GWA, lowest (below detectable limit) in SHD.

3.2 Characterization of starch-silver nanodichlorvos formulation

UV-VIS absorption spectra analysis

The spectra exhibits a strong peak at 419 nm, (Figure 2), which has been reported to be the characteristic of the Surface Plasmon Resonance (SPR) of silver nanoparticles (Saifuddin et al, 2011, Ihegwuagu et al, 2014). In metal nanoparticles like silver, there is free movement of electrons because the valence and conduction band lie close to each other, giving rise to surface plasmon resonance. SPR is the collective oscillation of electron of silver nanoparticles in resonance to light waves (Saifuddin et al, 2011). The colour of the composite was grey-black at the end of the synthesis.

Powder X-ray diffraction analysis

The typical XRD pattern of silver nanocomposite is shown in Figure 3. The pattern depicts diffraction peaks of 2θ values with slight shifts to 32.7 ^{o}, 46.5 ^{o}, 67.7 ^{o} and 76.8 ^{o} from values of 38.4 ^{O}, 44.4 ^{O}, 64.1 ^{O} and 77.7^{O}which can be indexed to reflections of (111), (200), (220) and (311) of pure silver crystals (JCPDS Card No. 04-0783),(Theivasanthi and Alagar, 2011). These shift maybe due to the presence of the components of dichlorvos in the nanocomposite crystals.

High Resolution Transmission Electron Microscopy (HR-TEM)

The size and shape of the AgSRF within the nanoacomposite were recorded by the HR-TEM as shown in Figure 4. The images depicts a spherical and well dispersed nanoparticles with size range of 23-35 nm (Akbari et al, 2011, Hamedi et al, 2012). Note the properly magnified bar size of 20nm making the image visualization very clearly (Bajpai et al, 2013). HR-TEM has been reported to be the best method of morphology determination (Akbari et al 2011).

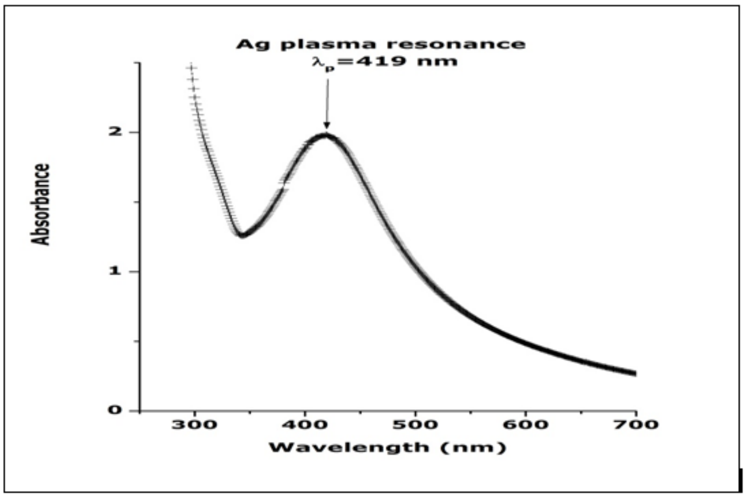

Figure 2: UV-VIS absorption spectra of silver nanoparticles-dichlorvos formulation (AgSRF).

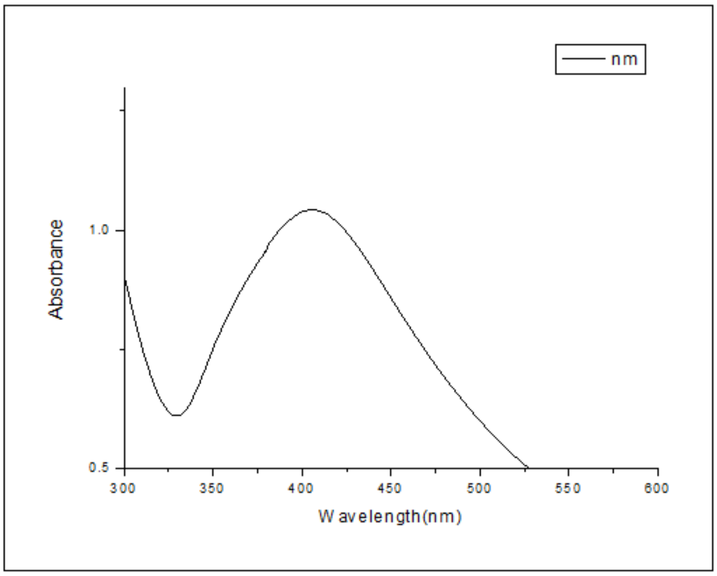

Figure 2: UV-Vis spectrum of nanoformulation

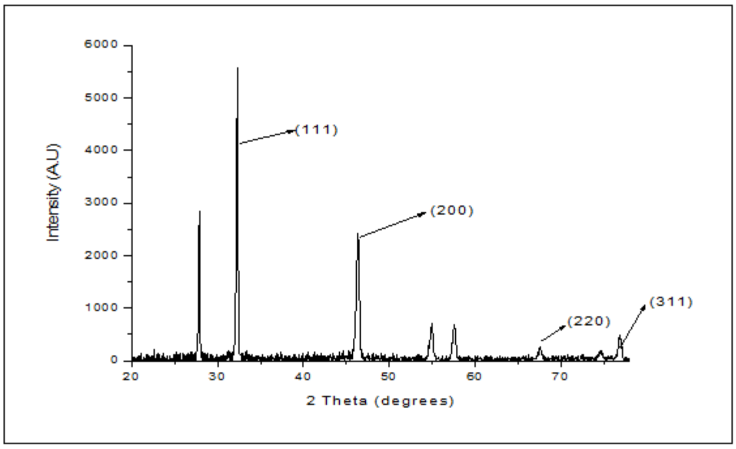

Figure 3: Powder X-ray pattern of silver nanoparticles-dichlorvos formulation

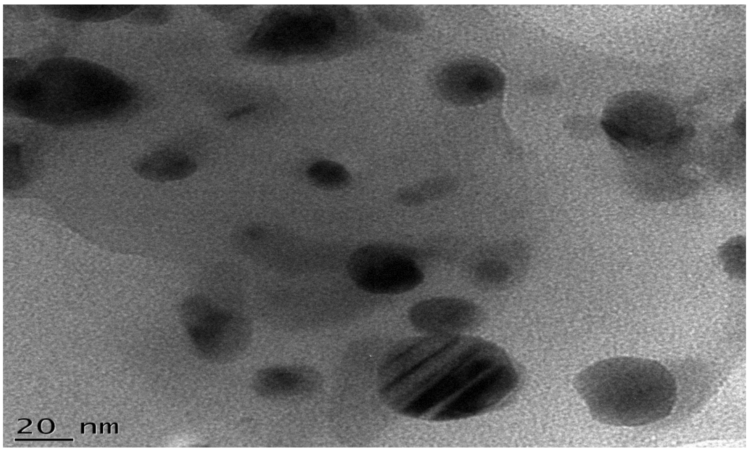

Figure 4: HR-TEM image of silver nanoparticles-dichlorvos formulation

3.3 Aqueous release of dichlorvos from nano formulation (AgSRF) in the soils

In the release studies, the AgSRFs had an enhanced release pattern in all SHD soil type more than the two soils. The cumulative release orderfor the soils was SHD (13%) > LTE (6%) > GWA (5%), (Figure 5), depicting the superiority of release profile in SHD soil over GWA and LTE. All had initial burst release in the first 4 hours and subsequently exhibited steady slow release, as reported in literature for different pesticides by various researchers (Kumar et al, 2006, Bajeer et al, 2012). The implication is that the formulation is able to eliminate existing pests in the first 4-6 hours and then maintain efficacy slowly for up to months (Tijani et al 2007, Onyido et al, 2012, Mohamed et al, 2014).

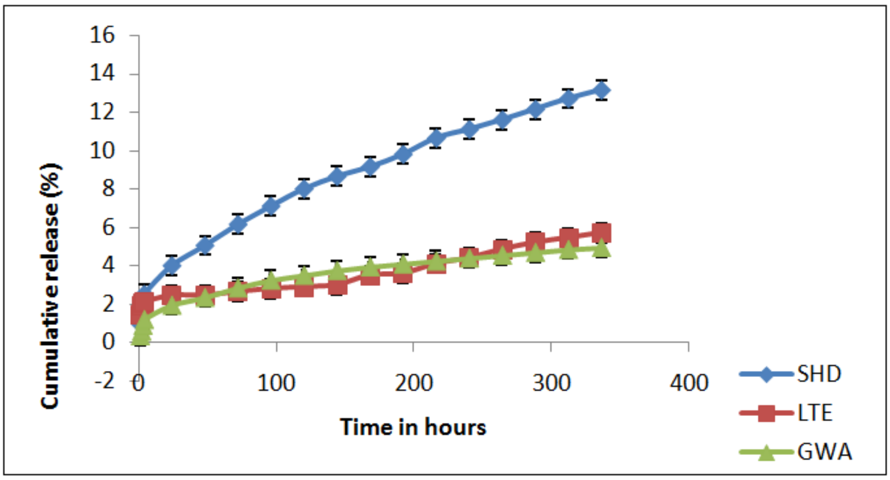

Figure 5: the cumulative dichlorvos aqueous release from nano formulations for soil types.

3.4 Insecticide leaching

The leaching patterns of the soils investigated depicted distinct differences across the formulations (Technical (Tech), commercial (EC) and silver slow releasenano formulation (AgSRF).The leaching medium was used to mimic rain. The time it took GWA soil to give out its first leachate of 4.0ml out of the 5ml of buffer (pH 6.5) poured in as leaching medium was 5minutes, SHD took 9 minutes to leach 4.5ml while LTE leached only 3.0ml at a time of 89mins. For different soil samples time (hours)was plotted against the amount of insecticide leached over ten rain incidentsand presented in Figures 6, 7 and 8. From the leach patterns, in terms of percent dichlorvos leached, the soil ranking is SHD (48.1%) > GWA (33.9%) > LTE (22.4%). Meaning the sandy-clay- loam leached most and the clay loam retained most. In all both release or leaching, the general trend that high acidity in soil sample favours low leaching and high adsorption was observed with LTE soil sample and this is in agreement with Bajeer, et al.(2012).Also the effect of pH on adsorption of pesticide in acidic soil has been reported to be more compared to basic soils. This played out in this study and reason was adduced to be due to the presence of a stronger cation exchange mechanisms favouring chemisorption, (Bajeer et al. 2012).Sheda (SHD) soil was sandy textured, low carbon content and low organic matter therefore low adsorption and higher leaching (Table 1). The soil with higher leaching has less adsorption, means that soil possesses light texture. Invariably, leaching and adsorption are inversely related to each other this is consistent with the reports of Alister, et al., (2011), Bajeeret al., (2012), Ebeling, et al., (2013). Formulation ranking across soils in term of percent dichlorvos leached shows Tech (42.2 %) > EC (42%) >AgSRF (19.9%). There was no significant difference between the leaching pattern of both Technical and EC treatments. The AgSRF formulation leached significantly lesser than both treatments (Figures 6-8).This trend is supported by the work of Johnson and Pepperman, (1996),where leaching of alachlor was less in controlled/slow release formulation than the technical and commercial. Also, Maqueda et al**, (**2008) recordedreduced leaching of metribuzin in the novel controlled/slow release formulation. In another, bentonite and anthracite in alginate-based controlled release formulations were found to reduce leaching of chloridazon and metribuzin in a calcareous soil by Cespades et al, (2013). The findings of Ebeling et al, (2013), that silver nanoparticles appear to aggregate in a salt solution rendering them less toxic to zebrafish may be the reason the formulation had the least leaching as it may have been aggregated or formed a silver chloride salt with some of the components of the insecticide, making it environmentally safe**.**

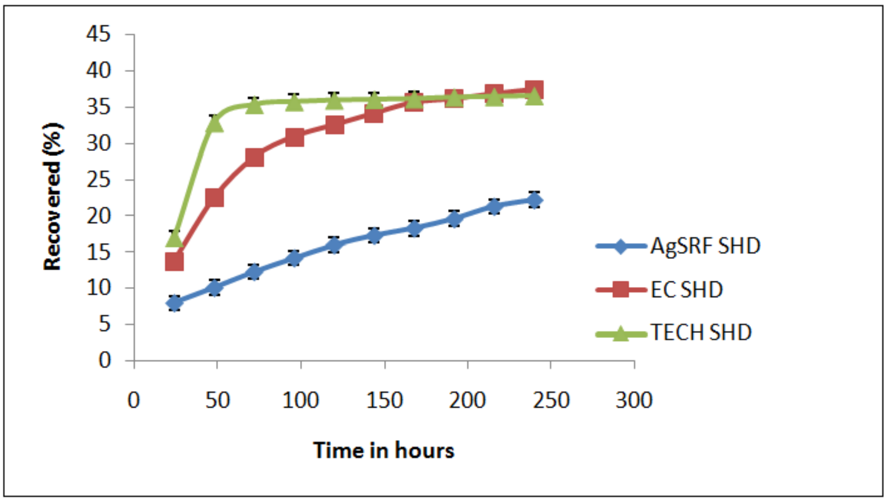

Figure 6: the cumulative dichlorvosleached for Technical, commercial (EC) and slow release nano formulations for SHD soil.

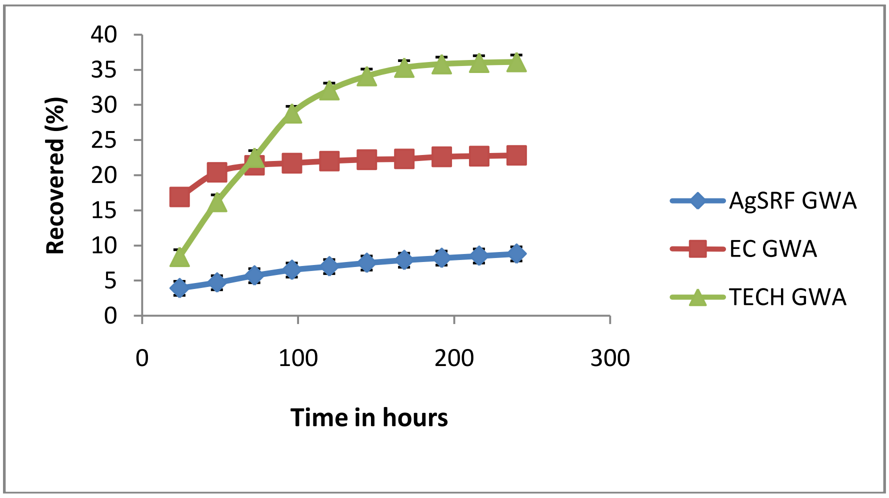

Figure 7: the cumulative dichlorvos leached for Technical, commercial (EC) and slow release nano formulations for GWA soil.

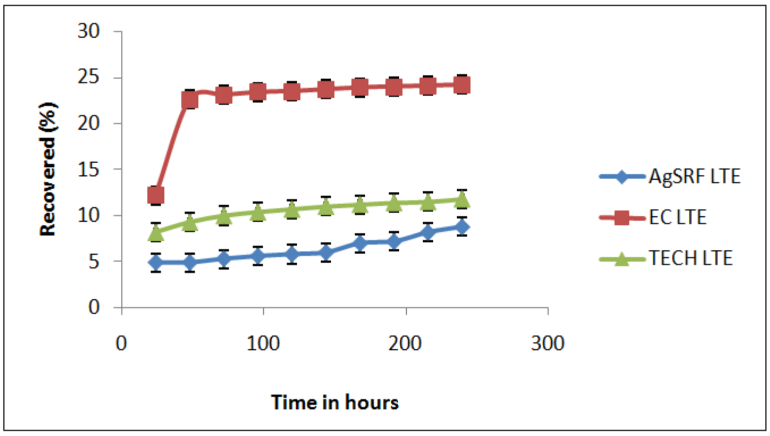

Figure8: the cumulative dichlorvos leached for Technical, commercial (EC) and slow release nano formulations for LTE soil.

3.5 Desorption patterns of the insecticide

Desorption is a key process affecting pesticide behaviour in soils and controls the predisposition of a pesticide to be degraded and/or leached at different times (Lima et al, 2010). The result of the desorption experiments (Figure 9) demonstrate the capacity of the soils to retain adsorbed DDVP after ten elution (mimicking rain) and about seven rinses. In this work, however, about 53% (AgSRF), 15% (EC) and 21 % (TECH) of the adsorbed insecticide was removed in the desorptive rinses. A significant amount of the insecticide was retained on the soil surface by AgSRF compared to the technical and EC forms. Although dichlorvos in the three formulations tended to decrease with number of rinses if leaching had continued.

Demonstrations of increased concentration of pesticide on the soil surface by several researchers are consistent with the findings of this study. Johnson and Pepperman (1996) found that about 39-54 % alachlor remained on soil surface in column experiment more than technical and commercial and was released gradually. Also, the mobility of metribuzin from control released formulations into soil columns of sandy soil was greatly diminished in comparison with commercial formulation (CF) (Maquedaet al, 2008).

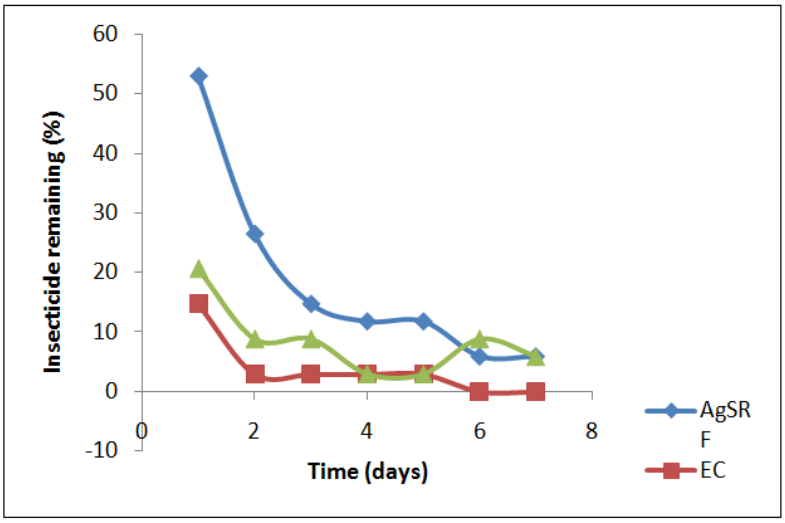

Figure 9: the cumulative dichlorvos desorbed for Technical, commercial (EC) and slow release nano formulations (AgSRF) in 7 days.

IV. Conclusion

The soils in the Gwarinpa and Sheda, Abuja, has pH following the order GWA > SHD > LTE in alkalinity and Cation Exchange Capacity while organic matter content followed the order SHD > GWA > LTE. A greater percentage of the applied dichlorvos in the column soil surface was retained by the AgSRF formulation than the technical and commercial (EC) formulations. Also, the AgSRF had a decreased leaching potential for dichlorvos in the three soils investigated. Hence an end to the ground water leaching potential of insecticides is in sight when above effects are combined. Result from the release study shows that the AgSRF had a slow and sustained release, (Figure 5), depicting the superiority of release profile in SHD soil over GWA and LTE, a similar trend observed in the leaching study. Retention of herbicide in the surface horizon improves efficacy against germinating weeds/ pests in this zone, it is available for pest/weed control in un- bound form and also the pesticide is prone to degradation in this biologically zone than subsoil (Johnson and Pepperman, 1996).In this present study, UV/Vis spectroscopy reveals the surface plasmon property, while the HR-TEM revealed the nano nature and size of the one-pot insitu synthesized/ encapsulated starch-silver nanoinsecticide formulation (AgSRF) (Bajpai et al ,2013).Mention of a product or trademark in this study does not constitute any preference to the exclusion of other products in Nigeria.

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