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Facile formulation of starch-silver-nanoparticles encapsulated dichlorvos and chlorpyrifos for enhanced insecticide delivery

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Abstract The facile formulation of starch-silver nanoparticles encapsulated dichlorvos and chlorpyrifos, respectively, was explored in this study with the view to develop a safer and more economical insecticide delivery system. The nanoparticles matrices were synthesized and the insecticides encapsulated *in situ* during the chemical reduction of silver nitrate by glucose employing direct heating. The starch-silver nanoparticles encapsulation of dichlorvos (ST-AgNP-VOS) and chlorpyrifos (ST-AgNP-FOS) were confirmed by UV-Vis spectroscopy and characterized by HR-TEM, EDX, SAED, FTIR, XRD and FESEM. The characteristic colour of AgNPs was observed and Surface Plasmon Resonance (SPR) of the materials was found to be in the range of 418-422nm. In addition, the XRD results revealed the silver identification diffraction peaks at 2θ angles in each formulation. Insecticide encapsulation efficiency was about 95% for ST-AgNP-VOS and 98% for ST-AgNP-FOS. Compared to control having no silver (NDVOS), both materials showed better insecticide loading. Their HR-TEM images indicated spherical natures of the materials with an average particle size range of 23nm–35nm. FESEM image showed spheres as well and a size close to that indicated by HR-TEM analysis. FTIR also confirmed the loading of dichlorvos and chlorpyrifos with additional peaks corresponding to them, compared to the insecticide-free starch. These nano-insecticide formulations were subjected to aqueous release studies. The result showed an enhanced release over the formulation without silver nanoparticles. It was concluded that this approach could be used to prepare slow release formulations of these insecticides, with the advantage of the silver nanoparticles also acting as anti-microbial agent. This current synthetic/encapsulation process can be readily applied to large-scale production.

Introduction

The use of excessive doses of pesticides poses many environmental risks to several ecosystems and, lack of full control over pesticide application to their target is reportedly responsible for the

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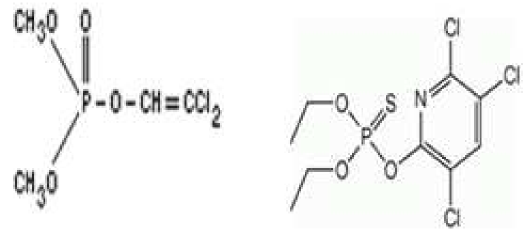
estimated 50% loss of the amount applied [1]. The presence of pests and weeds decreases agricultural crop production and has direct impact on food security. Insects are vectors of many diseases, and many others damage crop plantations or wood structures, causing serious health and economic losses. It is estimated that about 14-25% of total agricultural production is lost to insect pests [2]. It is, generally, accepted that a viable alternative way to surpass the predictable crisis in agriculture is to increase the crop yield by proper control of insect pests and weeds. The current way of surmounting this has been the use of conventional pesticides which in most cases are overused or lost to the environment leading to contamination. This bulk use of pesticides pollutes ground waters, sediments, soil, surfaces and plants, affects non-target organisms and ultimately poses a danger to humans.

In order to minimize these adverse effects in pesticide delivery a promising field has been opened by use of controlled release (CR) formulations, since they offer the potential of increased pesticide efficacy at reduced doses. CR formulations of pesticides have been proposed to produce a better spatial distribution of the pesticide on leaf surface, soil and water, which provides better efficiency. Furthermore, the use of nanoparticles for drug delivery has been well studied in pharmaceutics [3,4] and this is now gaining ground in agricultural sciences for slow or sustained release of pesticides [5, 6]. Nano formulations of pesticides forms present an attractive alternative as their effective concentration is much lower compared to that of the bulk materials and they can be formulated without the use of organic solvents [7]. They are mostly prepared as entrapments in biodegradable polymers like starch by various methods, to control rate of release, decomposition, leaching, groundwater contamination and other associated problems [8]. Thus, the use of nanoparticles-based formulations has offered another avenue for the efficacious delivery of pesticides.

For instance, pediculocidal and larvicidal activity of synthesized silver nanoparticles against the head louse *Pediculus humanus* and fourth instar larvae of *Anopheles subpictus and Culex-quinque fasciatus* [9]. Nanoparticles loaded with garlic essential oil are efficacious against *Tribolium castaneum* Herbst [10]. Nanotube filled with aluminosilicate can stick to plant surfaces, while ingredients of nanotube have the ability to stick to the surface hair of insect pests and ultimately enter the body and influence certain physiological functions [11]. Furthermore, the study of the dynamics of chlorpyrifos encapsulated in the blend of starch and alginate followed by crosslinking with $CaCl_2$ solution resulted in formation of spherical beads which showed controlled release property [12, 13]. Also it has been reported that pesticide nanoformulation showed less toxicity toward non-target organisms compared to the bulk or commercial formulations and therefore high specificity was observed [14]. This novel organophosphate pesticide formulation, therefore, presents safer, efficacious, lower dose, environmental friendly and economical choice respectively. Lee et al.,[15] reported that AgNPs possesses low toxicity to human cells, high thermal stability and low volatility. They found it to be cost-effective and also of importance as it may have potential as an anti-infective agent for human fungal diseases.

Dichlorvos, o-2,2-dichlorovinyl-o,o-dimethyl phosphate (DDVP; VOS) **(I)**, and Chlorpyrifos, o,o-diethyl o-3,5,6-trichloropyridin-2-yl phosphorothioate, (FOS) **(II)** are both chlorinated organophosphate insecticides that are extensively used in many countries mostly developing countries for controlling insect pests on agricultural, commercial, domestic, and industrial sites.



(I) (II)

Fig. 1: The molecular structure of dichlorvos (I) and Chlorpyrifos (II)

Compared to other insecticides, these two organophosphates (**I**) and (**II**) are generally preferred because of their wide range of bioactivity [12, 16 - 18]. DDVP alone had annual worldwide sales in 2003 of about 40 million U.S. dollars [16]. Their demand is high owing to the recent ban of some other popular organophosphates. Both insecticides like other organophosphates, show insecticidal action by the inhibition of the enzyme acetylcholinesterase, resulting in the accumulation of the euro-transmitter, acetylcholine, at nerve endings, resulting in excessive transmission of nerve impulses, which causes mortality in the target (mostly insect pests) [18 ,19]. Chlorpyrifos is a degradable molecule and breaks down in the environment when exposed to microorganisms, chemical reactions, and sunlight [19]. In view of the above, there is need to check their usage to a minimal level and prevent it from leaching into the environment (especially water bodies). The efficacy of pesticides (which include insecticides) depends mainly on their level of use which in turn depends on their market prices. Prices are particularly important since most of the pesticides are imported into the country (Nigeria) [20, 21]. With the low exchange rate of the Nigerian currency against major currencies of the world, the prices of the pesticides are becoming comparatively high. It is expected therefore that farmers would respond to changes in prices by adjusting the level of use of the resource alongside changes in its market prices. Some who cannot afford it may not use it leading to low yield and losses.

Also in Nigeria, it has been reported, [22] that about 15,000 metric tons of assorted pesticides (including dichlorvos and chlorpyrifos) are imported annually and recent studies carried out on 127 different food items revealed pesticide presence to be above maximum allowable concentration ranging from 1.2-2160�gkg^{-1}. Although there is a paucity of a reliable data base on past pesticide poisoning/spills as well as the absence of a thorough monitoring on the usage of these products, the occurrence of their residues in the environment has also been established [19]. This, no doubt has negative implications for the ecosystem and non-target organisms; this has become great concern requiring immediate intervention. One approach lies in employing pesticide delivery systems that minimize the amount used without loss of efficacy, such as has been demonstrated by slow-release formulations.

This study aimed to synthesize silver nanoparticles stabilized by abundant cassava (*Manihot esculenta*) starch as matrix for the encapsulation of **(I)** and **(II)** via a facile, cheap and reproducible method, characterize them as well as evaluate their ability to deliver the encapsulated insecticide active ingredient in a slow release manner into aqueous environment.

Experimental

Materials

Chemicals employed in this synthesis were purchased and used without further purification. Silver nitrate ($AgNO_3$), 98%, Sigma Aldrich, Germany, Glucose, was purchased from Finlab Chemical Company, Abuja, Nigeria. Dichlorvos (DDVP), 95% and chlorpyrifos from AgroChina Company, Shanghai. Native cassava starch powder was extracted from cassava tubers bought from Karmo Market, Abuja, Nigeria. All solutions were prepared using distilled water.

Cassava Starch Extraction

The native cassava starch was extracted from cleaned cassava tubers according to reported methods with modification. Visible dirt and contaminants were removed from the material, (1 kg), which were thoroughly washed, peeled and cut into pieces before suspending in water(1:3 w/v). This was ground in a mill with water and the homogenate filtered through muslin cloth. The filtrate was allowed to settle overnight. The supernatant was decanted, top layer discarded and the sediment (the resultant starch) was re-suspended in water (thrice) before final filtering and sun-drying of the resultant starch. The dried starch was homogenised with mortar and pestle, defatted and stored in cellophane wrapping [8, 20].

Synthesis of Starch- Silver nanoparticles-encapsulated dichlorvos (ST-AgNP-VOS) and chlorpyrifos (ST-AgNP-FOS):

Starch-silver nanoparticles-encapsulated dichlorvos and chlorpyrifos was formulated according to [24,26], with the modification that encapsulation was achieved *in situ* during the synthesis of silver nanoparticles by direct physical gelation. The synthesis was carried out via chemical reduction of silver nitrate by glucose as follows: To a mixture of 1% (0.06M) $AgNO_3$ and 0.2M glucose solution (1:3 volume ratio) in a loosely covered flask containing 1% starch dispersion (1g in 100ml distilled water), was added 1ml **(**0.0061M) dichlorvos and 1ml (0.001M) of chlorpyrifos respectively. This was stirred and heated at 80- 90^{o}C in a fume cupboard for 3 hours. The resultant complex was cooled and centrifuged at 11,000rpm for 20 minutes using Eppendorf 5417R micro-centrifuge. Subsequently, each ST-AgNP-VOS and ST-AgNP-FOS nano-formulations were 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 in the dark for further use and characterization. A similar procedure was performed for the preparation of the control (NDVOS and NDFOS) both of which had no $AgNO_3$ and glucose in their preparation.

Characterization of the ST-AgNP-VOS and ST-AgNP-FOS.

UV–Visible spectral analysis
The confirmation of the synthesis of nano particles was monitored with UV-VIS spectrophotometer (Agilent, Model 8453 Chemstation software). Aliquots (3ml) of the suspension, was measured to determine the Surface Plasmon Resonance absorption maxima with distilled water as reference.

Fourier Transform–infrared (FTIR) spectral analysis
The FTIR spectra were recorded with an ATR Spectrometer (Perkin Elmer Spectrum 100). The samples were scanned within 380 – 4000cm^{-1} range.

HR-TEM, EDX and SAED of ST-AgNP-VOS and ST-AgNP-FOS
Dispersed ST-AgNP-VOS samples in absolute ethanol were dropped onto coated copper grids and allowed the ethanol to evaporate. Micrographs were obtained using a High Resolution Transmission Electron Microscope (HR-TEM) (FEI TECNAI 02) having software TECNAI G^{2}. HR-TEM was equipped with an Energy-Dispersive Spectrum (EDX) as well as Selected Area Electron Diffraction (SAED) capabilities and the samples were analysed accordingly.

Field Emission Scanning Electron Microscopy (FESEM) of nano formulations of ST-AgNP-VOS and ST-AgNP-FOS
Field Emission Scanning Electron Microscope micrographs were taken on Zeiss Auriga FEG-SEM Model 55, operated at 10KV for high resolution imaging.

Powder X-ray Diffraction (PXRD)
The synthesized insecticidal nano formulations of dichlorvos and chlorpyrifos were structurally analysed using the Diffractometer, D8 Advance (by BRUKER AXS, Germany) and the XRD pattern analyzed according to JCPDs patterns.

Encapsulation Efficiency (E.E.)
Dichlorvos and Chlorpyrifos concentration in the supernatant after the centrifugation of the prepared nanosphere solutions were detected using the UV-VIS Spectrophotometer at 335nm (VOS) and 328nm (FOS). Encapsulation rate was calculated using the formula:

$$E.E\% = \frac{[(\text{Total insecticide added}) - (\text{insecticide in supernatant})]\text{x}100}{\text{Total insecticide added}}$$

Aqueous Release studies

The slow release studies of loaded nanospheres were carried out by placing samples of ST-AgNP-VOS and ST-AgNP-FOS of known weights (20mg) in a glass vial containing 15ml of phosphate buffer pH 6.5 at ambient temperature, respectively [25-26]. The set-up underwent gentle shaking and at specific time intervals, 3ml was withdrawn for analysis and this was replaced with a fresh 3ml of the medium to maintain sink condition. After syringe-filtering of the aliquot, UV-Vis spectrometer was used to study the release and related as concentration released via the calibration plot of DDVP and chlorpyrifos. This same procedure was performed for ST-AgNP-FOS and the controls without silver nanoparticles.

Statistical Analysis
In order to check the reproducibility of the results, all the experiments were performed at least three times (n = 3) 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.

Results and discussion

It needs to be noted that in each nanopesticide formulation, the overall cost is minimal since its only little quantity of the silver salt solution that is reduced to colloidal silver metal (unreactive state) and the concentration of silver metal in the final product is below the World Health Organization (WHO)'s No Observable Adverse Effect Level (NOAEL) of silver salt and metal. Which is pegged to be

5µg/kg/bw/d, and in humans is put at 0.39mg/person/day for adult of 60kg (the sum of all exposure routes), [27,28].

Physico-chemical characteristics of the ST-AgNP-VOS and ST-AgNP-FOS

UV–Visible spectroscopy

The optical spectrum of the nanoformulation is shown in Fig. 2a and 2b. This is the first confirmation of silver nanodichlorvos and nanochlorpyrifos. The obtained silver nano-insecticide both showed a broad peak at 418nm and 422nm respectively in the spectra which are due to the excitation of Surface Plasmon Resonance (SPR) of silver atoms. This has been reported to describe the collective excitation of conduction electrons in a metal [29].

During their synthesis, three processes occurred in the reaction mixture (equations (1) – (3): (i) reduction of the silver ion to silver nanoparticles during exposure to the glucose solution (ii) encapsulation of dichlorvos and chlorpyrifos insecticides in to the nanoparticles so formed and (iii) the inclusion/sorption of the particles in the starch matrix which had been gelatinized due to the heat applied.

$$Ag^{+}_{(aq)} + starch_{(aq)} \longrightarrow [Ag(starch)]^{+}_{(aq)} \quad (1)$$

$$[Ag(starch)]^{+}_{(aq)} + C_5H_{11}O_5CHO_{(aq.)} \longrightarrow [Ag^{0}(starch)]_{(gel.)} + C_5H_{11}O_5COOH_{(aq.)} \quad (2)$$

$$[Ag^{0}(starch)]_{(gel.)} + a.i. \longrightarrow [Ag^{0}(starch).a.i.]_{(s.)} \quad (3)$$

The dispersion of the silver ions in the starch matrix (Eq. 1) forms a stable gelatinous complex $[Ag(starch)]^{+}$ which goes on to react with glucose (aldehyde, reductant) to form Ag nano particles (embedded in the starch) and gluconic acid (Eq.2). In this milieu, the active ingredient (a.i. = chlorpyriphos or dichlorvos) gets included/sorbed to the matrix surfaces.

This is a one-pot, economical method of formulation. It is well reported that reduction of silver ions in aqueous solution to silver nanoparticles is accompanied by colour change (yellowish-brown or greyish) due to excitation of surface plasmon vibrations in silver nanoparticles [24, 30 - 33].

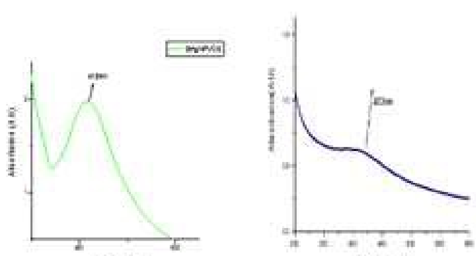


Fig. 2: The UV-VIS Spectrum of starch-nanosilver dichlorvos and chlorpyrifos formulations.

FTIR spectroscopy (FTIR) spectra of the starch silver nanoparticles were recorded identified the functional groups of glucose and starch involved in the reduction and capping/stabilization as shown for ST-AgNP-VOS (a) and ST-AgNP-FOS (b) formulations and native starch (c), Fig.3 and table 1. The broad and strong band at 3,344 cm^{-1} which is due to the O-H stretching vibration. This was shifted from 3328 of the O-H stretching vibration of the native starch. Particularly, ST-AgNp-VOS nanoparticles loaded DDVP (Figure 3a) has shown all the above characteristic peaks with a slight shifts from the peak 1627cm^{-1} to 1563cm^{-1} corresponding to C=O stretching. Peaks at 2,915 cm^{-1} corresponded to the asymmetric and symmetric bending vibrations of the methylene groups. Fig. 3a and 3b supports the presence of silver Nano composites loaded films due to the presence of additional peaks at 1404 cm-1 and 842 cm-1 corresponding to insecticides [34]. All these indicate that silver nanodichlorvos as well as nano- chlorpyrifos was attached to the functional groups present in starch. The shifting of the peak is due to formation of co-ordination bond between the silver atom and the electron rich groups (oxygen/carbonyls) present in starch. This causes an increase in bond length and frequency [29, 32, 33.]

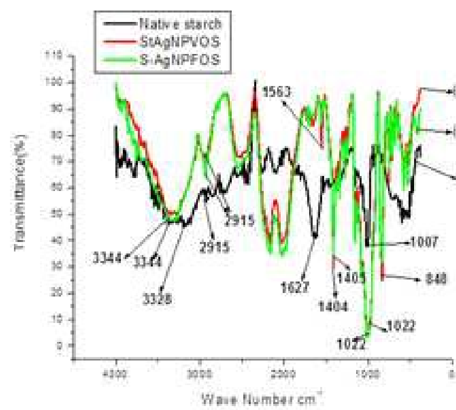


Fig.3. FTIR Spectra of Starch -Silver nano dichlorvos(a), nano-chlorpyrifos formulations (b) and Native starch (c)

Table 1. FTIR Functional groups analysis

Vibrational Assignment/ Functional group	Observed wave number (cm^{-1}) in STAgNPVOS	Observed wave number(cm^{-1}) in ST-AgNPFOS	Observed wave number(cm^{-1}) in Native starch
OH	3344	3344	3328
CH_3	2915	2915	2915
C=O	1563	1690	1627
Peak	1404	1405	Nil
C-O-	1022	1022	1007
New peak(maybe due to VOS or FOS)	848	832	Nil

HR-TEM micrograph of the ST-AgNP-VOS and ST-AgNPFOS

The HR-TEM of ST-AgNP-VOS image (Fig.4a) reveals spherical particles of average size range 23-30 nm, majority of the spheres are in this size range. With the average particle size obtained from these micrographs being about 23.2 nm. Fig. 4b is the micrograph of ST-AgNP-FOS also spherical and sized about 25-35nm. It is obvious that these nanoparticles are monodisperse. HR-TEM micrographs are the best method of determining morphology of nanoparticles and the obtained spheres are in agreement with previous reports [32-33].

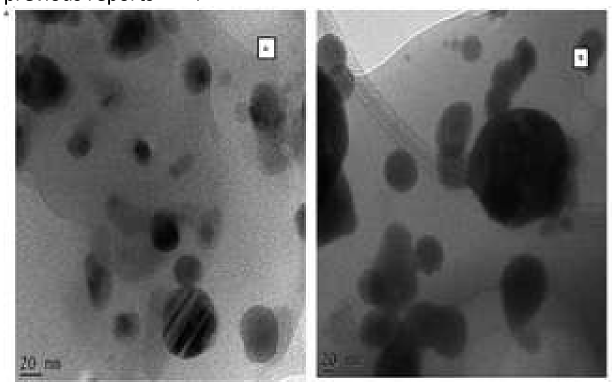


Fig. 4. The HR-TEM of ST-AgNPVOS(A) and S-AgNPFOS (B)

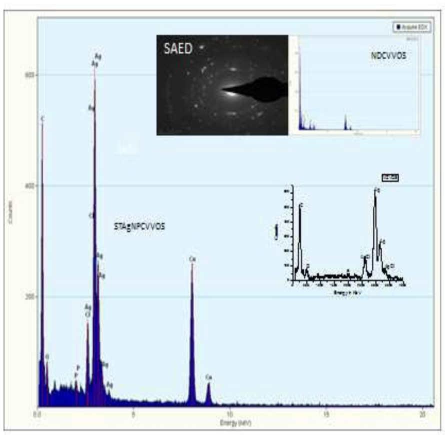


Fig.5 Showing the elemental analysis (EDX) and inset shows the SAED of nanocomposite and control (NDCVOS) no silver.

EDX spectral analysis revealed the strong signal in the silver region and confirmed the formation of silver nanoparticles as well as the chloride from the insecticides (Fig.5). The typical optical absorption band peaked nearly at 3 KeV confirming the metallic silver nanoparticles due to SPR [25, 34]. SAED patterns depicted in Fig.5 shows bright dots, indicating that these nanoparticles may be crystalline in nature. Usually, the arranged rings can be attributed to the diffraction from the (111), (200), (220), and (311) planes of Face- Centered Cubic (FCC) silver [34].

Field Emission Scanning Electron Microscopy (FESEM)

Further characterization with Field Emission Scanning Electron Microscopy (FESEM) was used to analyse the surface morphological characteristics which revealed uniform spherical morphology without any aggregation. The particle size was found to be 34nm for ST-AgNP-VOS (Fig.6a). Such size distribution analysis primarily confirms that the particles are well dispersed with minimal aggregation. Results of the surface morphology of ST-AgNP-FOS using FESEM depicted in Fig.6b indicate spherical monodisperse particles of average size of 27.78nm. Both grain sizes are little larger than those obtained from the HR-TEM analysis. This may be due to the fact that metallic nanoparticles are constantly nucleating and also the larger size may also be due to the tendency of nanoparticles to agglomerate owing to their high surface energy [35].

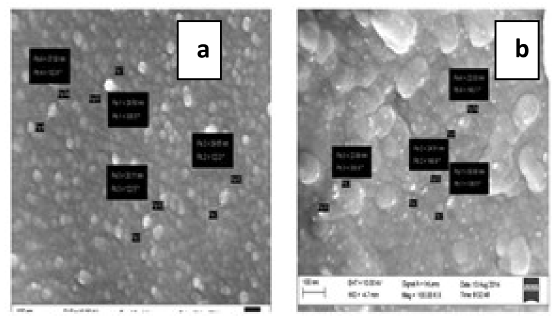


Fig.6: FESEM micrographs of starch- silver nano dichlorvos (a) and Chlorpyrifos (b).

Powder X-ray Diffraction (PXRD) Analysis

The Powder X-ray diffraction patterns of the starch silver nano-organophosphate (dichlorvos and chlorpyrifos) formulations is shown in Fig.7 a-b. All the reflections corresponding to silver metal with face centred cubic symmetry are depicted with slight shift and new reflections which may correspond to the insecticidal components are evident. Importantly, the 2θ values of starch still exist. X-ray diffraction study further confirmed the synthesis of nanoformulations. While the reflections of silver nanoparticles were indexed as (111), (200), (220) and (311) with the corresponding 2θ values of 38.4 ^{O}, 44.4 ^{O}, 64.1 ^{O} and 77.7 ^{O} respectively (JCPDS Card No. 04-0783), the nanoformulated insecticide presented prominent peaks at 32.1^{O}, 46^{O}, 67^{O} and 77^{O} revealing shifts in the peaks corresponds to (111), (200), (220) (Fig.7 a-b). However, almost all diffraction peaks were broad indicating that the crystallite size may be very small respectively.

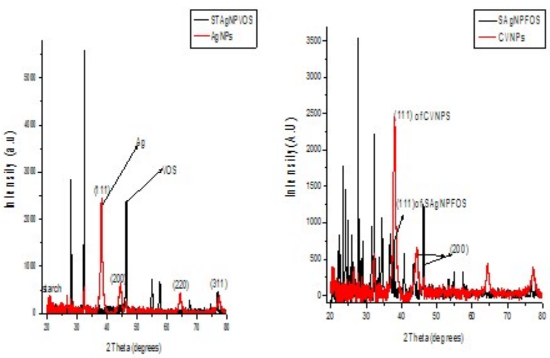


Fig. 7. XRD patterns of both silver nanoparticles and starch silver nano-formulation of the insecticides.

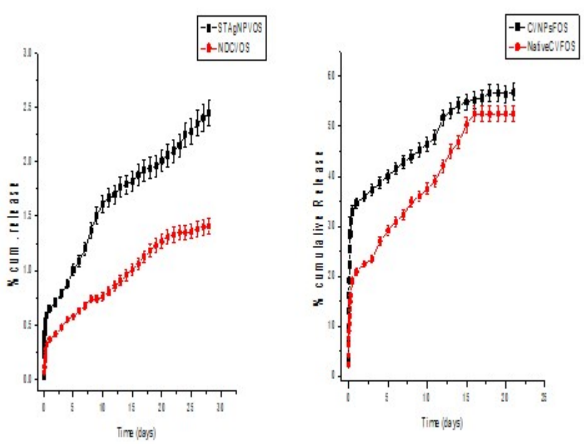


Fig. 8: Release profile of nanosilver-chlorpyrifos (ST-AgNP-FOS) in 21days (with error bars).

Table 1. Encapsulation efficiency of nano-formulations and control.

S/N	Formulation	%Amount Insecticide(w/v)	%Matrix (starch)w/v	%Encapsulation Efficiency (E.E.)
1	STAgNPCVVOS	1.34	1	95
2	NDCVVOS	1.34	1	78
3	SAgNPCVFOS	0.2	1	98
4	NDCVFOS	0.2	1	60

Insecticide Encapsulation Efficiency (E.E.)

The principle of active ingredients loading on silver nanoparticles is surface adsorption[34]. It was observed that increasing quantity of insecticide made little change on encapsulation efficiency (E.E.) of the silver nanoparticles. The percent encapsulation efficiency is shown in Table 2. The content of active ingredient was determined from calibration curves for dichlorvos and for chlorpyrifos. The prepared samples were visually observed and found to be coloured greyish for nanodichlorvos and blackish-brown for nanochlorpyrifos respectively. Those of control (without $AgNO_3$ and glucose were whitish in colour) signifying no silver nano-formulation in them. The presence of silver in the starch nanoparticles increased encapsulation efficiency as shown when compared with the control (free insecticide formulation without silver). When 1.34% (w/v) of dichlorvos was added with 1% matrix, the percent insecticide loading was 95% in nano formulation (ST-AgNP-VOS), but same quantity in the control (NDCVOS), gave E.E. of 78%. This was, similarly, observed for chlorpyrifos (an E.E. of 98% compared with only 60% E.E. in control). This enhanced insecticide loading could be due to the reported large surface area as a property of silver nanoparticles [3, 24 - 26].

Aqueous release behaviour

The UV-Vis spectrophotometer was used to analyse the time-dependent release of the insecticides from their nano-formulations (ST-AgNP-VOS and ST-Ag-NP-FOS) in water. Insecticide concentration was correlated via absorbance of formulation's aliquot release per time. The accumulated release of dichlorvos was found to increase with contact time (Fig. 8 a-b). There was an initial fast release in both silver nano-formulations and the control and this was followed by a subsequent steady release. This has been considered advantageous as it will readily be available to kill existing pest before planting (insects) and subsequently kill and/or inhibit new infestation [35,36]. The ST-AgNP-VOS showed a fast release from 0 minute to 250 minutes (4.2hours), followed by a slower but steady one from 350 minutes. Notably the nano silver formulation showed an enhanced release over the formulation without silver nanoparticles NDCVOS (Fig. 8 a-b). While a total release of about 25.0 % was released in 24 hours by nano silver dichlorvos, the NDCVOS released 18. 0 %. This is in agreement with Namasivayam et al[35], who reported an improved slow release and herbicidal activity of silver nanoparaquat. It is conceivable that the presence of nano-silver in the starch matrix opens up the intricate starch structure, by intercalation, with the effect that the diffusion/migration path length within the matrix becomes less tortuous, making the release of the active ingredient easier and faster compared to the control.

After 21 days, there is an implication that the ST-AgNP-VOS may still be releasing into months while the control seem to be approaching exhaustion (Fig. 8a). This is in agreement with a report [9, 20] that its release could last for months and even years making our nanoformulations timely to offer safer doses in a sustained manner.

Environmental and health implications of the use of these nanoformulations

Silver nanoparticle (AgNPs) has been under a great deal of scrutiny from when its use became popular. Nowack *et al.*[37] has wondered why no any known harmful impact on humans or the environment has been reported. Ebeling *et al.*[38] and SCENIHR[39] found that silver nanoparticles appear to aggregate into a salt solution rendering them less toxic to zebra fish and some aquatic life than would be expected. Further researchers found that plants in a system could help decrease the toxicity of AgNPs (if any) because plants release dissolved organic matter which can bind with Ag ions[40]. Additionally other researchers suggested that the chemistry of the nanoparticle capping agent plays an important role in the fate and transport of AgNPs and environmental factors such as pH, ionic strength, and electrolyte composition can help predict the fate and transport of AgNPs[41]. In a freshwater system, researchers found that sediments accumulated most of the ceria nanoparticles used in their aquatic system[42]. The European Scientific Committee on Emerging and Newly Identified Health Risk[39] found out that Ag-NPs undergo several transformations when it is released into the environment. Apart from aggregation and agglomeration, the important ones are dissolution and subsequent speciation, such as the formation of silver chloride and silver sulphide. Silver sulphide is particularly important because it is highly stable.

In consideration of the foregoing non-conclusive evidence on the environmental impact of AgNPs, there is need to investigate the environmental dynamics of AgNPs in the context of our nanoformulations, before any position can be taken on their environmental impact post application.

Conclusions

This study has established that loading of the insecticides; *in situ* during silver nanoparticle synthesis stabilized by starch was viable, and occurred with success, producing nanostructured material. Their encapsulation efficiency showed enhanced loading compared to the controls. Their characterization UV-VIS spectrophotometer, Fourier Transform–infrared ,High Resolution Transmission Electron Microscope, Field Emission Scanning Electron Microscope, Powder X-ray Diffraction, Energy-Dispersive Spectrum and Selected Area Electron Diffraction) proved that the spherical, medium sized (23-34nm) silver nanodichlorvos and nanochlorpyrifos insecticides were formed and aqueous release studies conducted in buffer medium revealed that both silver nanodichlorvos and nanochlorpyrifos (ST-AgNP-VOS and ST-AgNP-FOS) could achieve highly effective, long-acting, sustained release lasting for 21days. This formulation will produce synergetic effect to combat the adverse effect of the conventional or her bulk insecticide to the environment. It can also offer some antimicrobial activity depending on the application and target [29]. Scaling up production is attainable.

Acknowledgements

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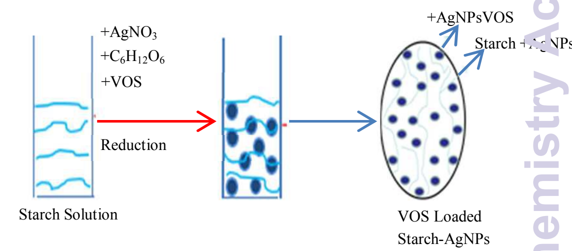
+AgNPsVOS
Starch +
$+AgNO_3$
$+C_6H_{12}O_6$
+VOS
Reduction
Starch Solution
VOS Loaded
Starch-AgNPs