

**EFFECT OF TEMPERATURE, PH AND ADDITIVES ON THE RATE OF  
DICHLORVOS INSECTICIDE RELEASE FROM STARCH SILVER  
NANOPARTICLES ENCAPSULATE.**

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**SUMMARY**

The encapsulation of widely used organophosphorus insecticide in Nigeria; dichlorvos, was achieved in situ on to cassava starch nano silver particle matrices with the aim to produce more effective, cheaper and safer slow/controlled delivery formulation than conventional pesticide formulations over a longer time. The starch -silver nanoparticle matrices was synthesized during the chemical reduction of silver nitrate by glucose employing direct heating. The starch-silver nanoparticles encapsulation of dichlorvos (CVNPsVOS) was confirmed by UV-Vis spectroscopy and characterized by HR-TEM, FESEM, FTIR, and XRD. The characteristic Surface Plasmon Resonance (SPR) at 418nm. The XRD results revealed silver diffraction peaks at 2θ angles in the formulation. Encapsulation efficiency was 95% for CVNPsVOS better than control having no silver (NativeVOS). Nano-formulations showed an enhanced aqueous release over the control. Their HR-TEM and FESEM images analysis indicated spheres with an average particle size range of 23nm–35nm. FTIR also confirmed the loading of dichlorvos with additional peaks corresponding to them while Control had none. The effect of temperature on release showed (20 °C > 30 °C), pH (4.0 >9.0 > 6.5) and additives (Tween 20, Triton X-100 and peanut oil) showed an order TW (50%) >PO (48%) >TX (41%). This current synthetic/encapsulation process can be scaled up as slow release formulations with silver nanoparticles acting as anti-microbial agent also.

**Keywords:** Insecticide, release, starch, nanoparticle, Dichlorvos

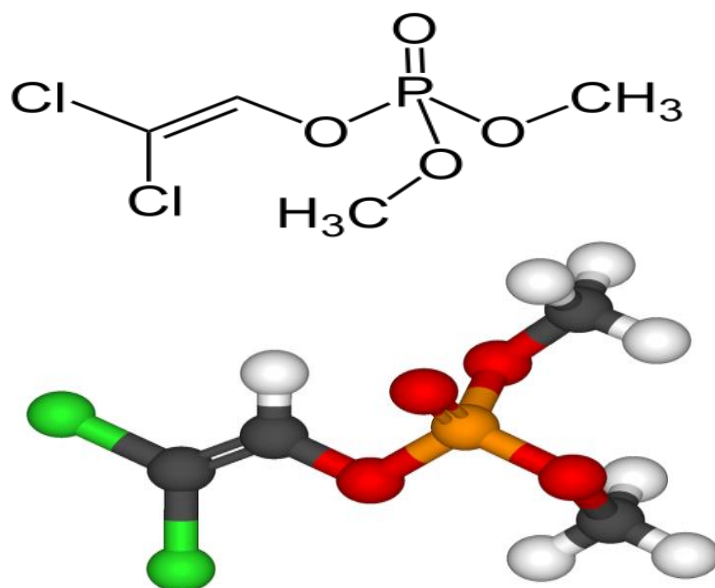
The presence of pests and weeds has continually decreased the crop production and threatens food security globally. Another truth is that the conventional method of pesticides application allows for the use of excessive doses of insecticide inputs and sometimes several applications in the life span of the crop. This makes room for losses which finds its way into the environment, water bodies and even undue exposure of the farmer. Thus, a novel method of combating the challenges associated with conventional pesticides is the use of nanopesticides (Alexandre *et al.*, 2011). Nano pesticides are nano formulation that combine the nanometer size range (Adetunji and Ugbenyen, 2011) and several surfactants, polymers (organic), and metal nanoparticles (inorganic). They are sometimes a viable and cheaper alternative way to surpass the foreseeable crisis in agriculture and environment degradation.

Nanotechnology is emerging as a highly attractive tool to achieve this goal. Slow release technology has been developed in the drug industry since 1960 in order to combat the side effects caused by administering high doses of conventional drugs and at the same time to maintain an effective level of drugs in the body. Applying the same principle in agriculture, has received attention during the last two decades to develop suitable controlled release pesticides for use in the soil and on foliage to reduce; pesticide application rates, pesticide levels in the environment, pesticide toxicity and to extend pesticide residual activity.

Furthermore, it is noteworthy to mention that nanomaterials could also be exploited to improve structure and function of pesticides by increasing solubility, enhancing resistance against hydrolysis and photodecomposition, and/or by providing a more specific and controlled-release toward target organisms (Gao *et al.*, 2011; Mishra *et al.*, 2015; Grillo *et al.*, 2016).

Dichlorvos, o-2,2-dichlorovinyl-o, o-dimethyl phosphate (DDVP; VOS) (Figure 1) 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; Nuruzzaman *et al.*, 2016).



**Figure 1:** Molecular structure of dichlorvos, O-2, 2-dichlorovinyl-O,O-dimethyl phosphate (DDVP) (FAO, 2009).

## MATERIALS AND METHODS

### Chemicals and material

Chemicals used in this study were purchased and used without further purification. Silver nitrate (AgNO<sub>3</sub>), 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<sub>4</sub>H<sub>7</sub>Cl<sub>2</sub>O<sub>4</sub>P ). A commercial Dichlorvos Emulsifiable Concentrate (EC) formulation (Delvap 1000EC)) 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 starch was extracted and defatted according to reported methods with modification using native cassava (Ihegwuagu *et al.*, 2014).

### **Synthesis of dichlorvos loaded slow release formulations of starch nano silver**

The employment of direct physical gelation method during the chemical reduction of silver nitrate by glucose, according to Saifuddin *et al.*(2011) and Al-Hmoud *et al.* (2011) gave rise to Starch-silver nanoparticles-encapsulated dichlorvos in-situ by. A complex of 0.06M AgNO<sub>3</sub> 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 20 minutes using Eppendorf 5417R micro-Centrifuge. Subsequently, the CVNPsVOS nano formulation underwent precipitation with the addition of acetone (30ml), re-centrifugation at 6000rpm for 5 minutes and sediment oven-dried at 40 °C for 24 hours. 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<sub>3</sub> and glucose just the conventional DDVP in native starch.

### **Characterization techniques**

The confirmation of the synthesis of the silver nanoparticles loaded with dichlorvos was done with UV–Visible spectrophotometer. However, appearance of sharp plasmon resonance band around 400 nm confirmed presence of the mono dispersed AgNPs, UV-visible spectrophotometer Agilent, Model 8453 Chemstation software was used for spectral recording. High Resolution Transmission Electron Microscope (HR-TEM) FEI TECNAI 02) was applied in the morphological characterization of the nanoinsecticide CVNPsVOS. Fourier Transform–infrared (FTIR) spectral analysis was recorded with an ATR Spectrometer (Perkin Elmer Spectrum 100). The samples were scanned within 380 – 4000cm<sup>-1</sup> range. Synthesized samples were structurally analysed using

Diffractionmeter D8 Advance, by BRUKER AXS (Germany), XRD pattern was analysed according to JCPDs patterns.

## **Aqueous release studies**

### **Release in water**

The studies of the slow release profile of loaded nanospheres were carried out according to (Oyido *et al.*, 2012). The sample weighing 20mg was placed in a glass vial containing 15mL of buffer at ambient temperature. The set-up underwent slight shaking and at time intervals, 3mL for study was withdrawn and this was replaced with a fresh medium (3mL) to maintain sink condition. The time intervals were, 0, 5,10,30,60, 120, 180, 240, 300, 720, 1440, 2880 minutes up till 21 days. Then it was spectrometrically assayed for amount released with UV-VIS at their wavelengths. This was related to amount released via the calibration plot of each insecticide. Data obtained was average of duplicate studies from in aqueous insecticide release studies and was plotted as percent cumulative amount of release versus time.

The release % was calculated using the formula described by Alexandre *et al.* (2011) below:

$$\text{Release \%} = \left( \frac{\text{Released insecticide}}{\text{Total insecticide}} \right) \times 100\%$$

### **Effect of pH on aqueous release**

The pH effect on the release pattern was investigated for all nano-insecticide formulations in the starch using different pH, where the release medium pH was maintained at 4.0, 6.5 and 9.0. This was carried out at the ambient temperature for 18 days. The absorbance of the resulting solutions was measured with UV-Vis spectrometer.

### **Effect of temperature on aqueous release**

The temperature of optimised release medium was investigated between ambient (20°C) and an elevated temperature of 30°C. This was monitored in an electrically operated water bath (Julabo

P Labortecnik, Germany) for 14 days. The absorbance of the resulting solutions was measured with UV–Vis spectroscopy. Tests were carried out in duplicate.

### **Effect of additives on aqueous release**

The effect of additives on release pattern was investigated specifically to monitor for a change on the initial burst release, according to (13). The choice of non-ionic surfactant was informed by report of Yeo and Park (2004), that non-ionic surfactants retard the fast release of active ingredient. Three surfactant additives were monitored by adding them to the release medium at pH 6.5. These were Tween 20(polylobate 20), Triton X-100, and peanut oil. The release profile was monitored for 14 days using same method as section 2.3.1. Then, 0.1mL of each additive was dropped into the release medium and pattern monitored respectively.

### **Statistical analysis**

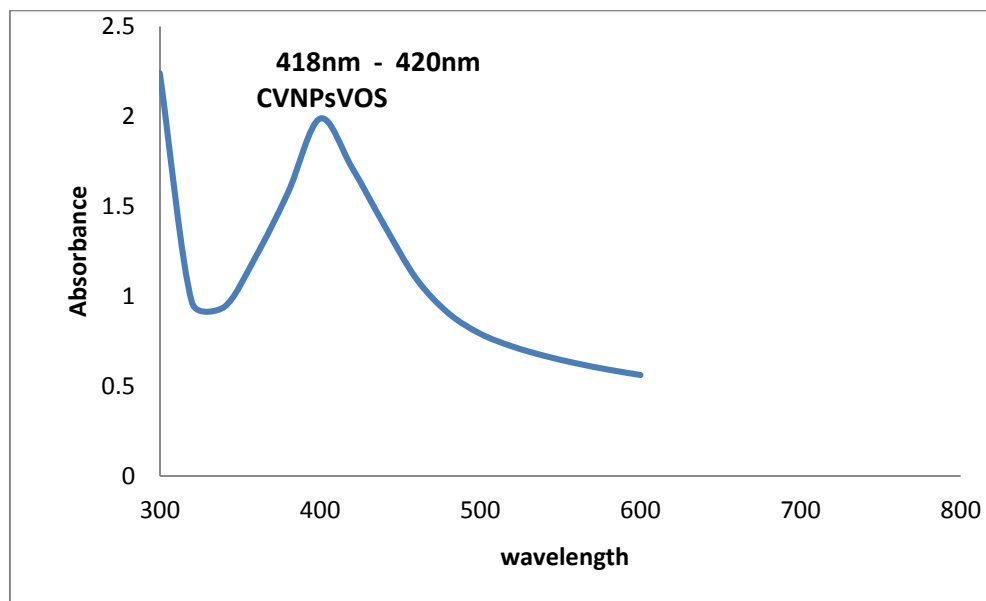
In order to check the reproducibility of the results, all the experiments were performed at least two times (n =2) and the data summarized have been expressed as means  $\pm$  s.d..

## **RESULTS**

### **Instrumental analysis of slow release nano formulations (SRNF)**

#### **UV visible spectroscopy of SRNF**

The optical spectra of the nano-formulations of the insecticide dichlorvos (CVNPsVOS) was determined with UV-Vis spectrometer. The spectrum is shown in Figures 2. This is the first confirmation of silver nanodichlorvos and the obtained silver nano-insecticides showed broad peaks at 418nm for CVNPsVOS



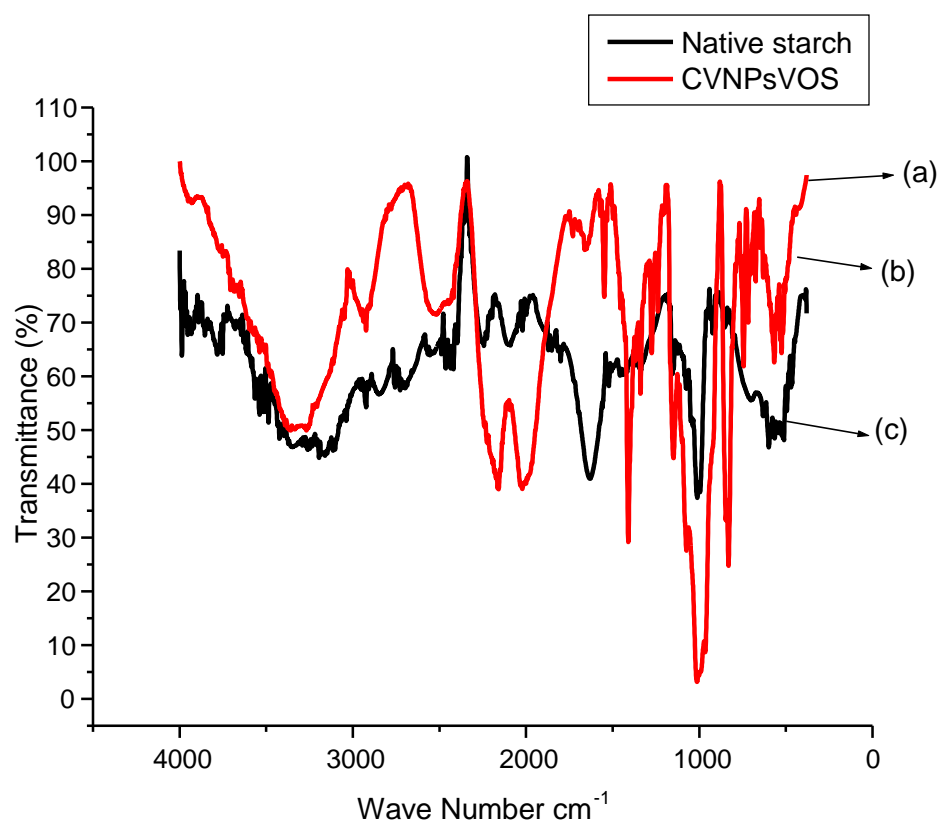
**Figure 2:** The UV-Vis spectrum of CVNPsVOS.

#### **Fourier transform - infra-red (FT-IR) spectroscopy**

The characteristic features of FT-IR spectra of the loaded Slow Release Nano-Formulations (SRNF) are depicted in Figure 3 for dichlorvos composites (CVNPsVOS). Also a summary of the functional groups was presented in Table 1. The Spectra of the SRNFs are almost similar to those of the native (Table 1). However, in the composites, the O-H stretching vibration bands shifted to  $3354\text{ cm}^{-1}$ (CVNPsVOS).

**Table 1:** FT-IR Functional Group Analysis for Slow Release Nano Formulations and native starch

Functional Group	Wave Number (cm <sup>-1</sup> )CVNPs VOS	Native starch
O-H	3354	3328
C-H	2946	2930
C=O	1648	1631
C-O-C	1156	1147
C-O	1003	1011
Gluconic	833	-
Ag	748	-



**Figure 3:** The FTIR spectral of Slow Release Nano formulation CVNPsVOS and Native starch

### **High resolution transmission electron microscope (HR-TEM)**

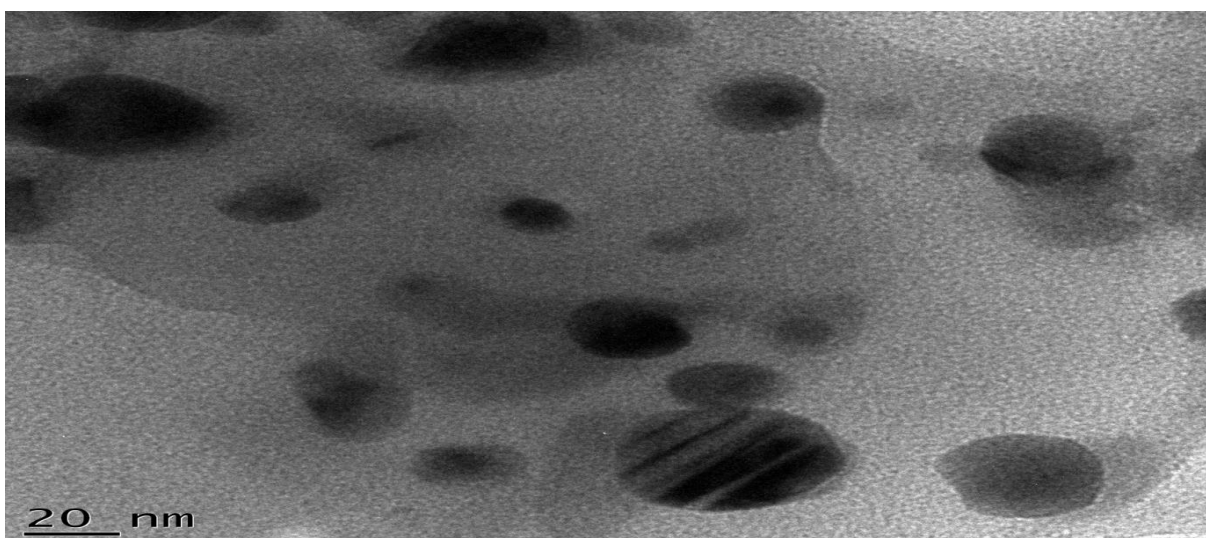
The HR-TEM micrographs (Figure 4a) revealed that generally particles are spherical in shape. The average size range for CVNPsVOS nanoparticles was 23-30nm, majority of the spheres are in this size range but average size obtained was about 23.2nm.

### **The field emission scanning electron microscopy (FESEM)**

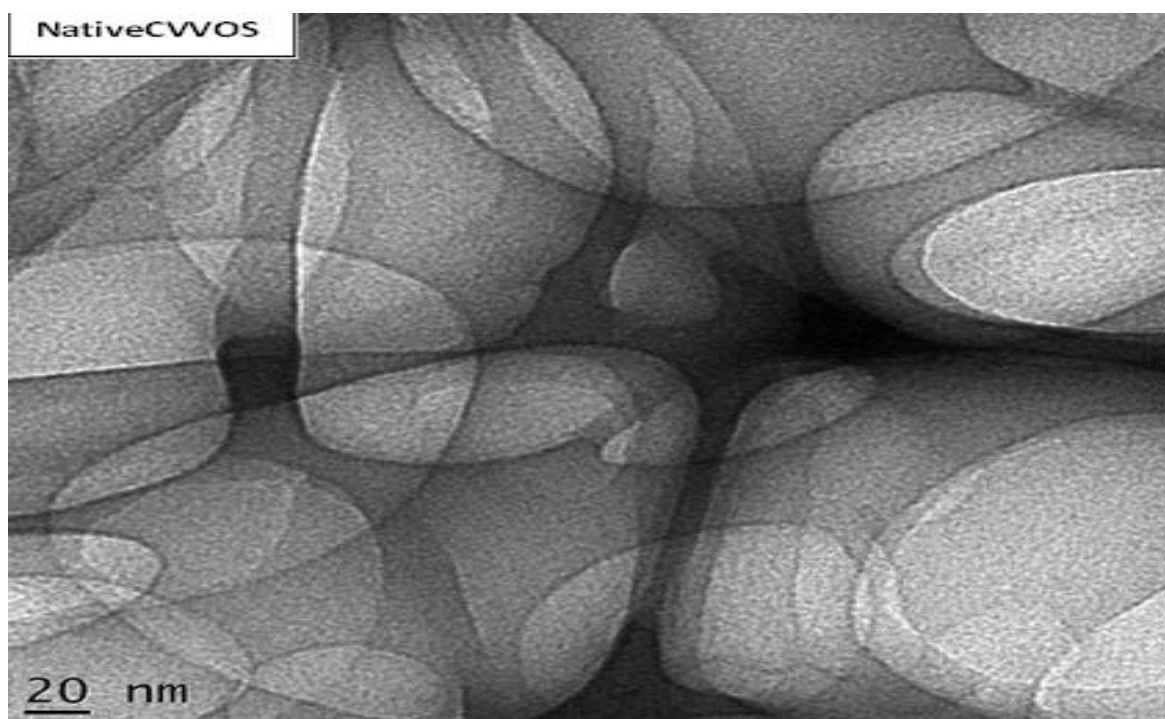
Field Emission Scanning Electron Microscopy (FESEM) was used to analyze the surface morphological characteristics of both formulations. The micrograph revealed uniform spherical morphology without any aggregation. The particle size was found to be 34nm for CVNPsVOS (Figure 5)

### **Aqueous release studies**

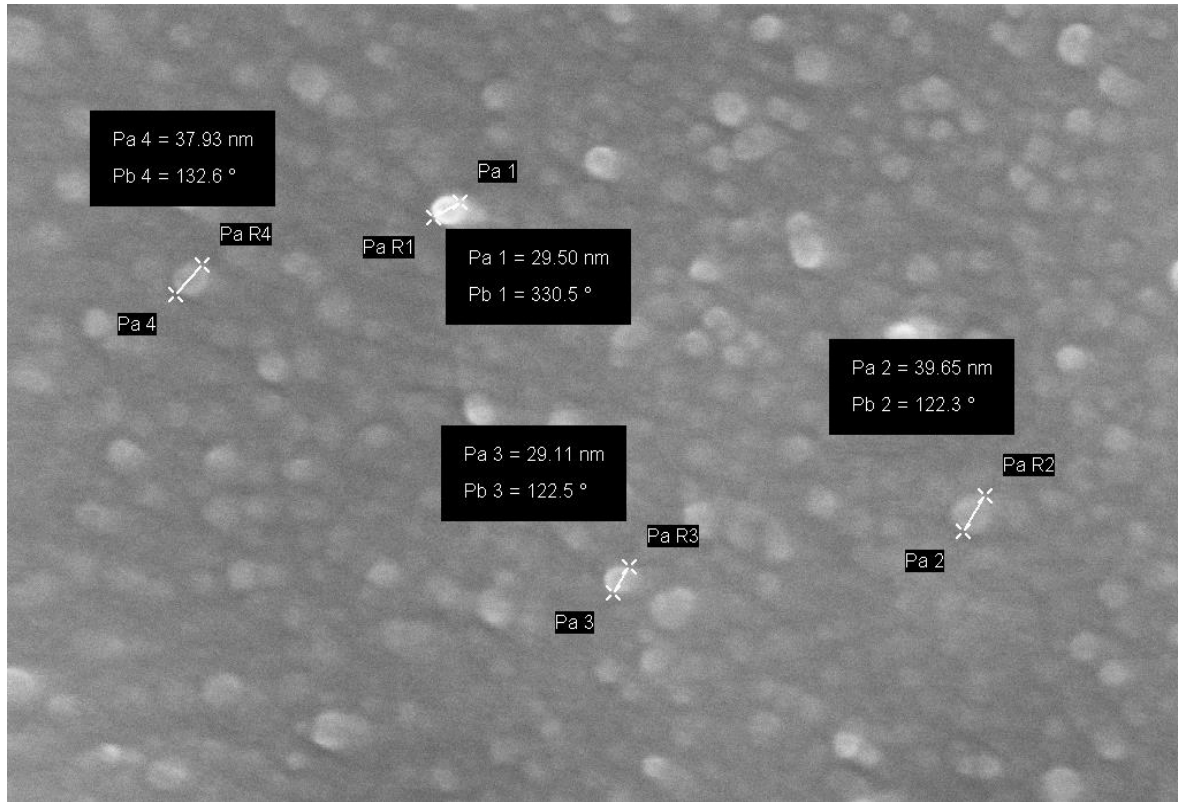
The release behavior of the Slow Release Nano- Formulations (SRNF) of the organophosphate insecticide active ingredients (a.i) namely; Dichlorvos (VOS), encapsulated in silver nanoparticles (AgNPs) using starches of cassava (CV). The amount of a.i released per time was detected using a UV-Vis spectrophotometer. Results of the release in water and the effects of additives, temperature and pH are presented.



**Figure 4a:** HR-TEM Image of CVNPsVOS



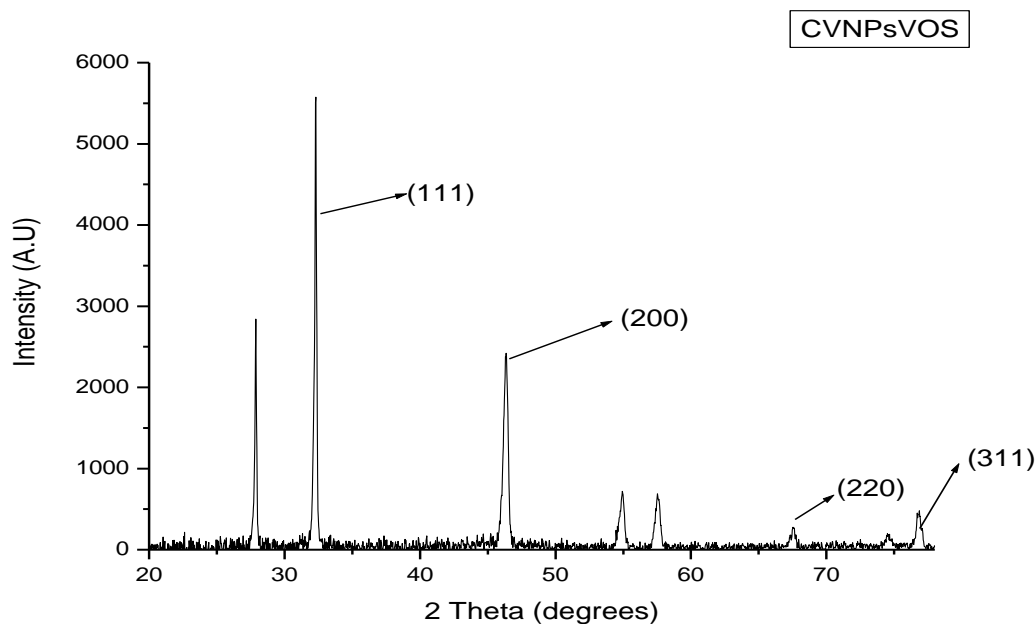
**Figure 4b:** HR-TEM Image of Native CVOS



**Figure 5:** The FESEM micrograph of the CVNPsVOS

### X-ray diffraction (XRD)

The diffraction peaks of silver appeared in both XRD pattern thus indicating their crystalline nature. In the XRD pattern of nano composite it was obvious that starch peak is not lost in the synthesis. The composite exhibited diffraction peaks at  $2\theta$  values of (111), (200), (220) and (311) with the corresponding  $2\theta$  values of  $38.4^\circ$ ,  $44.4^\circ$ ,  $64.1^\circ$  and  $77.7^\circ$  with slight shifts. For CVNPsVOS, the peaks shifted to  $33^\circ$ ,  $46.2^\circ$ ,  $66.5^\circ$  and  $77.09^\circ$  (Figure 6). Peaks can be indexed to reflections of (111), (200), (220) and (311) of pure silver crystals (JCPDS Card No. 04-0783), (Thwala, 2012). These shift maybe due to the presence of the components of dichlorvos in the nanocomposite crystals.



**Figure 6:** PXRD Patterns of Starch Silver Nano-Dichlorvos Formulation (CVNPsVOS)

**Dichlorvos release pattern in the matrix (CVNPsVOS).**

The UV-Vis spectrophotometer was used to analyze the timely release of the nano formulations CVNPsVOS, and that of native starch formulation (NativeVOS) in water respectively (Figure 7). Insecticidal concentration was correlated via absorbance of SRNF's aliquot release per time. The cumulative release percentage was calculated using initial insecticide (dichlorvos) concentration and the release at specified time and this was monitored for 21 days. The accumulated release of the insecticide (dichlorvos) was found to increase with contact time. The amount released in 24 hours in cassava matrix CVNPsVOS was 10% and in 504 hours (21 days) it released 31% free active ingredient. The NativeCVOS had a lower release of 6 % in 24 hours and 20 % in 504 hours (21 days).

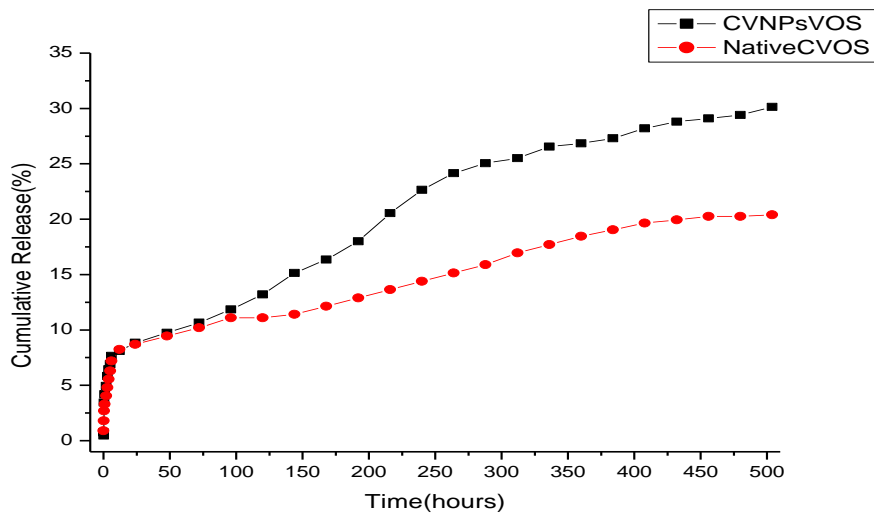
**3.2.2 Enhanced release factor (ERF)**

The enhanced release factor of nanoparticle formulations over native starch formulations was calculated according to the equation below, for the composites the result is shown below also. This enhanced release was observed after a passage of time when the burst release effect was over for all matrix.

$$ERF = \frac{\%Release\ in\ nanoparticle}{\%Release\ in\ native\ starch}$$

Result of Enhanced Release Factor of Nano Matrices over Native Matrices

Matrix	Enhanced Release Factor
CVNPsVOS	1.55



**Figure 7:** Release of Dichlorvos in 21 Days for Cassava Compared to Native Matrices in Water.

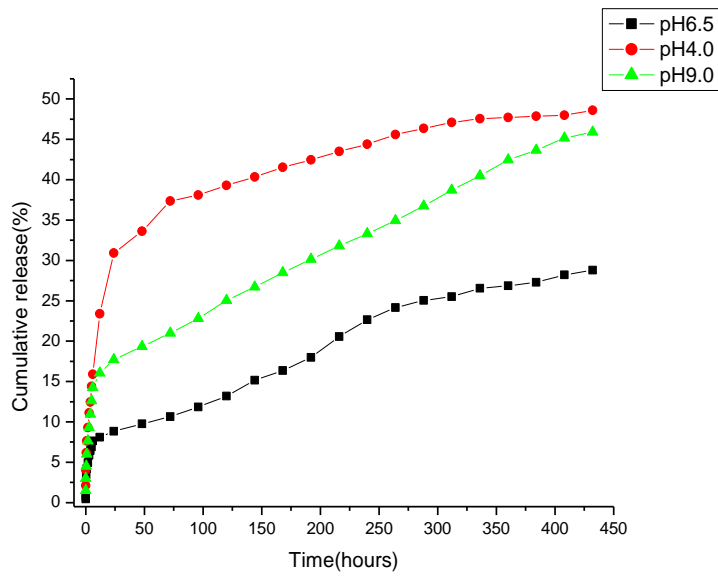
### **Effect of pH on the nano insecticide Release**

In order to investigate SRNFs' release behaviour in different environments, three buffers were considered; acidic (4.0), alkaline (9.0) and almost neutral pH (6.5). The effect of buffer pH: 4.0, 6.5, and 9.0 were investigated and assessed by UV-Vis spectrophotometry. This was monitored for up to 18 days (432 hours). Their release profiles up to 432 hours of incubation period were depicted in Figure 8. The release of dichlorvos at pH 6.5 had the lowest release of 29%; this was followed by pH 9.0 with a total release of 46%, while pH 4.0 showed the highest release of 49% for the period of 432 hours (Figure 8).

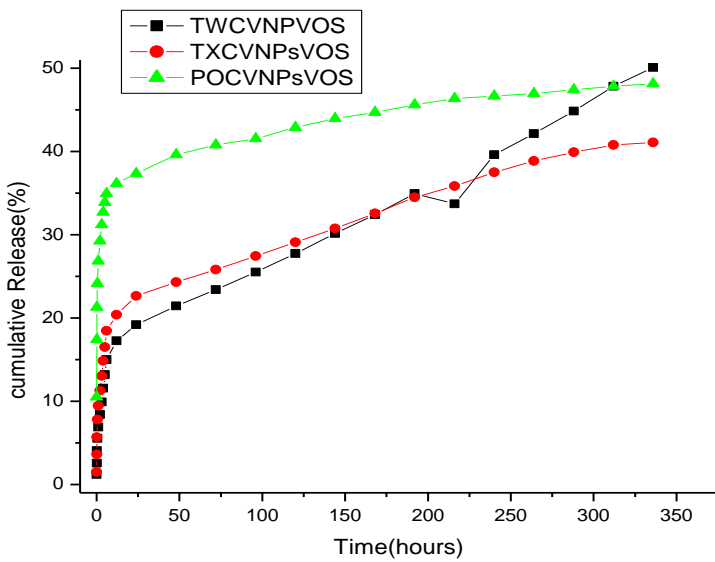
### **Effect of additives on release pattern of SRNFs (VOS)**

The effect of additives into release media of the two insecticidal nano formulations were monitored for 336 hours (14 days) using buffer of pH 6.5 at ambient temperature. The results in Figure 9, depicted the pattern of release the three additives Tween 20 (TW), Triton-X100 (TX) and Peanut oil (PO) impacted on the SRNFs. The order of release effect on VOS formulation was TW (50%) >PO (48%) >TX (41%), (Figure 9). Interestingly, there was an initial burst release.

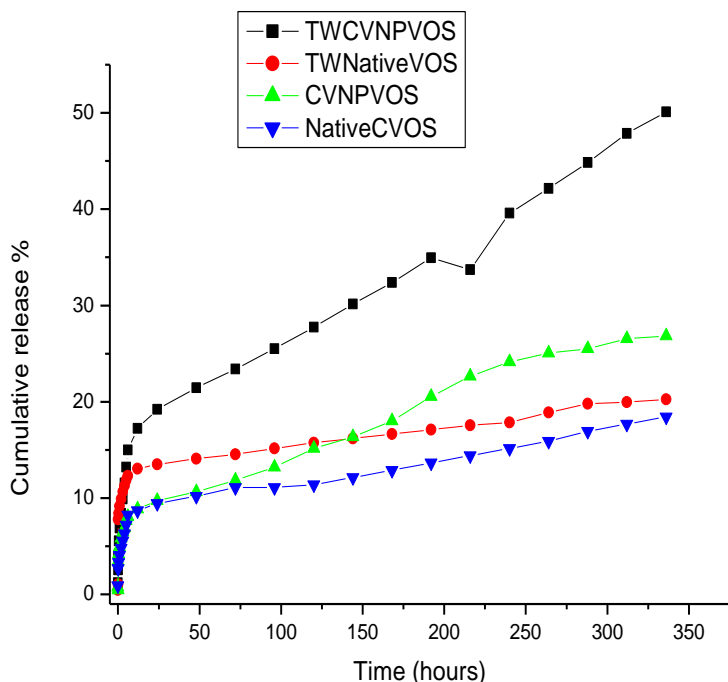
A comparison was done between SRNF VOS and NativeVOS, with TW added to both release media. It was found that nano formulations still had an enhanced release of 50 % against 20 % of the native starch formulation (Figure 10).



**Figure 8:** Effect of pH on Nano Dichlorvos Release



**Figure 9:** Effect of Additives on Dichlorvos Formulation Release in 336 Hours

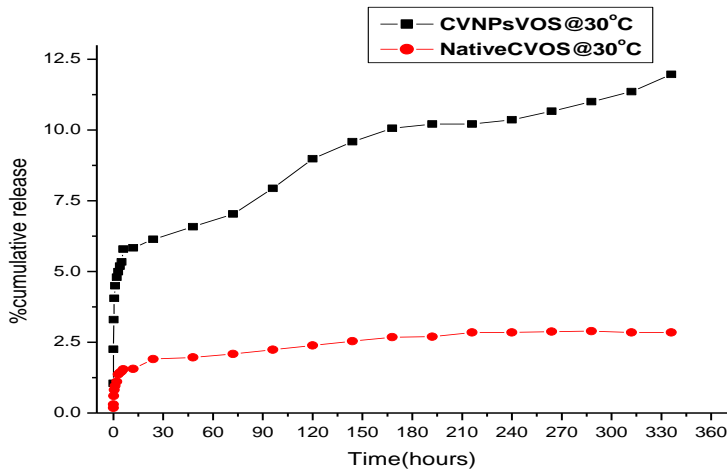


**Figure 10:** Comparison of the Effect of Additive (Tween 20) on Composite and Native Formulation.

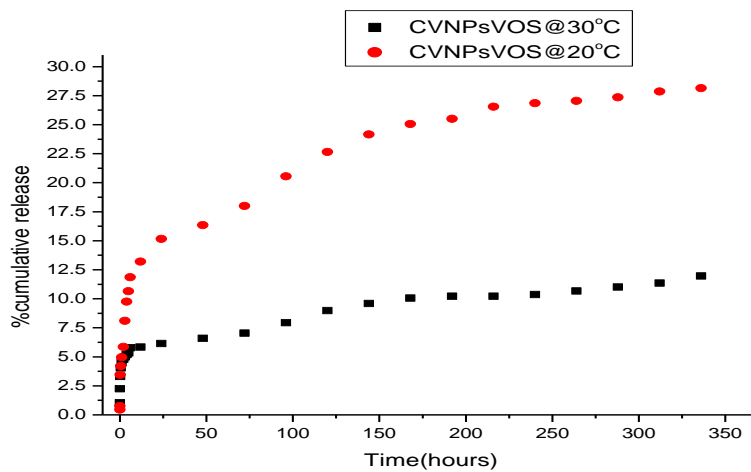
### **Effect of temperature on the SRNFs' release pattern**

Temperature effect on the release profile of insecticide (VOS) was monitored with cassava matrix at temperature of 30°C in comparison with the release at ambient temperature of 20°C. The pattern showed the slow release nano formulations (SRNFs) having enhanced release over the native matrix, (Figures 11). Result was similar to that obtained at ambient temperature (20°C) shown earlier (Figure 7). It was observed that the nanoparticles releases were in a slower manner. In Figure 11, VOS SRNF released 5.2% of a.i in the first 24 hours and was characterized with initial burst release also. It finally released 12% in 336 hours very much more than the 3% released by the native formulation at same temperature.

Furthermore, the release at 20°C in dichlorvos SRNF, was found to be higher than that released at temperature of 30°C, (Figures 12). This did not follow known trends.



**Figure 11:** Effect of temperature on Dichlorvos formulation release over native in 336 Hours (14days)



**Figure 12:** Effect of Temperature on Dichlorvos Formulation Release Pattern in 336 Hours (14 days).

## **DISCUSSION**

### **Aqueous release studies**

An important object of the present study was to study the release of an active agent from swellable and dissolvable polymeric matrix at nano scale and comparison to native matrix. Insecticidal release from nanoparticles is usually a biphasic phenomenon although on some occasions a triphasic profile is also seen. Firstly, there is an initial rapid removal of the insecticide from nanoparticles possibly related to loss of insecticide associated loosely on the surface of the nanoparticle. This initial release is rapid and uncontrolled and is termed the 'burst release' (Aydin and Pulat, 2012). Most particles reported in the literature are prepared using either interfacial deposition or emulsification methods; however, physical and chemical methods also show this initial release. The active ingredient loosely associated with the surface may occur due to the escape of insecticide during the organic solvent evaporation phase towards the external medium, and once the organic solvent evaporates there is re-adsorption of the a.i on the nanoparticle surface. After the surface component release is complete, there is a slower release of insecticide through the nanoparticle matrix (Namsivayan *et al.*, 2014). Generally, as mentioned in other reports (Ajiboye, 2012; Namsivayan *et al.*, 2014), there are mainly two release mechanisms from polymeric nanoparticles: diffusion through the micro channels that were formed during nanoparticles preparation and polymer erosion. In this study, the initial burst release effect is probably dominated by diffusion, rather than polymer erosion which are in line with the report of Ajiboye (2012). Here the release pattern of the SRNFs of the insecticides in comparison with the native composites was same (Figure 7), an initial fast release in both silver nano-formulations and the native and this was later followed by a slower and steady release. This trend has been reported to be advantageous as it will readily be available to kill existing pest (insects) before planting (Pratibha *et al.*, 2008) and still goes ahead to kill and inhibit new infestation. The CVNPsVOS showed a fast release from 0 minute to 250 minutes (4.2 hours), followed by a slower but steady one afterwards. Notably the nano silver formulation showed an enhanced release over the native formulation without silver nanoparticles native CVOS (Figure 7). This is in agreement with Do

(2004), who reported an improved slow release and herbicidal activity of silver nanoparaquate formulation. Also, the introduction of silver has helped to nanosize starch thereby increasing surface area, hence enhancing release. Noteworthy is the fact that after 21 days, there was an indication that the SRNFs of VOS may still be releasing into months while the native seems to be approaching exhaustion due to the near uniformity of its profile. This is in agreement with the report of Chen (2004) that the release of these insecticides especially dichlorvos could last for months and even years making the nanoformulations timely to offer safer doses in a sustained manner. Elsewhere, it was reported that dichlorvos's high volatility property coupled with persistence contributes to its efficacy in malaria vector control (Fishel and Ferrell, 2010).

The enhanced release factor calculated and presented in Table 2 showed that dichlorvos nano composites had higher values of enhanced release factors than matrices in relation to native matrix.

### **Effect of pH on release study**

As shown in Figure 8, both composites ST-AgNPVOS showed an initial burst release of insecticides in a period of 0 - 12hours for all pH release media. With pH 6.5 showing the lowest release in the first 24 hours for the composite, pH 4.0 exhibited the highest release also in 24 hours (Figure 8). This initial rapid release, later gave way to the slower releases as shown in the plot. At pH 4.0, the release rate was well higher or enhanced than the other two pH release media throughout the experimental days. The difference in release rate could be attributed to the enhanced solubility of nano dichlorvos at pH 4.0 (acidic medium), since pH has an effect on solubility due to its influence on ionization of the substances (Mehta *et al.*, 1994). However, a closer look at the graphical representation revealed that at pH 4.0, the release was actually a sustained plateau while at pH 9.0; the release is on a steady increase. A report by Jin *et al.* (2011) concluded that some pesticides, particularly organophosphates and carbamates insecticides, undergo a chemical reaction in the presence of alkaline water (water that has a pH value greater than 7). The reaction known as alkaline hydrolysis, reduces the effectiveness of the pesticide's active ingredient. They

added that the speed with which the breakdown occurs depends on the specific chemical properties of the pesticide.

### **Effect of additives on release pattern of SRNFs of VOS**

One of the goals in development of polymer micro or nano encapsulation systems is to reduce the initial burst and achieve a constant release rate thereafter (Aydin and Pulat, 2012). Burst release is due to poor control over diffusion - based release and the degree of initial burst from the micro particles depends on the ability of the polymer matrix to encapsulate the active ingredient, thereby making it unavailable for immediate diffusion (Bajpai and Likhitar, 2013). For this reason, efforts to reduce the initial burst have attracted many researchers (Aydin and Pulat, 2012; Qiu *et al.*, 2014). In this study, effect of additives on release profile was studied. Three of them studied were Tween 20 (TW), Triton-X100 (TX) and Peanut oil (PO) were all added to release medium and monitored for effect. It was observed that their burst release times were in the range of 0-4 hours. For dichlorvos, TX released 17 % a.i in 3 hours, PO released 35 % of a.i in 4 hours. TW had the lowest as it released 13 % in 3hours (Figure 9). Even though they reduced time of the burst release from 12 hours to 4 hours, they released far more a.i in those short time making them less economical to the nano insecticidal formulation and so much of encapsulated a.i is being washed off early.

### **Effect of temperature on release pattern**

At both low and elevated temperatures, this study observed better release rates from silver nano insecticide formulations over that of native (Figures 11 &12). Interestingly, release at ambient temperature of 20 °C was more than that of 30°C respectively. This trend is contrary to the general observation that increase in temperature leads to increase in rate of reaction and subsequently increase in release of active ingredient as swelling of matrix is expected to be increased (Rama *et al.*, 2014). Qiu *et al.* (2014) reported that at low temperature (15- 20 °C), agglomeration trend of silver nanoparticles weakens; meanwhile the structural regularity degree and the dispersion of

particles improved, and the average particle size may begin to vary. With an increase in temperature to about 30 °C, they said particle size reduces (shrinkage), although may demonstrate good monodispersity. This latter part of their findings is in agreement with Rama *et al.* (2014) who found that increase in temperature leads to possible shrinkage of matrix (hydrogel) as it tries to maintain 20% of its structural weight in aqueous environment. This maybe the reason our findings showed a lower release at a higher temperature suggesting a possible shrinkage

## **CONCLUSION**

The application of pesticides is a must for an agriculture based economy nation, to enable her feed her growing population with food and fiber. Most farmers know that it is economical to use pesticides to increase crop yield. The high cost and environmental problems associated with application of conventional pesticides at very high rates makes it justifiable to continue research on slow release formulations. Nanotechnology application in agriculture and food systems is still at the nascent stage and a lot more applications can be expected in the years to come. Effect of pH on release showed acidic (pH 4.0) to have the highest release pH 6.5 depicted the lowest rate.

Effect of three additives (Tween 20 (TW), Triton-X100 (TX) and Peanut oil (PO)) on release medium showed a reduction in the number of hours for the burst release from 12 to 4 hours, but they released far more active ingredient in those short time making them less economical.

At both low and elevated temperatures, this study observed better release rates from silver nano insecticide formulations over that of native. Release at ambient temperature of 20°C was more than that of 30°C, which may be due to weakening of agglomeration trend of silver nanoparticles around 15-20°C and possible matrix shrinkage at higher temperature.

It is in this regard that Nigeria needs to key in to nanotechnology, an emerging alternative technology with essential benefits to improve socio-economic development and transform important sectors like agriculture and medicine. Nanotechnology holds the promise of controlled

release of agrochemicals and site targeted delivery of various macromolecules needed for improved plant disease resistance, efficient nutrient utilization and enhanced plant growth.

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*EFFECT OF TEMPERATURE, PH AND ADDITIVES ON THE RATE OF DICHLORVOS INSECTICIDE RELEASE  
FROM STARCH SILVER NANOPARTICLES ENCAPSULATE.*

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