

KINETICS AND EQUILIBRIUM STUDIES ON THE ADSORPTION AND DESORPTION PATTERN FOR DICHLORVOS INSECTICIDE ON STARCH STABILIZED SILVER NANOPARTICLES

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ABSTRACT

In this study, the ability of starch nano-silver particles (CVNPs) to adsorb Dichlorvos (VOS) from aqueous solution was investigated through batch equilibrium experiments. Cassava starch stabilized silver nanoparticles were prepared by chemical reduction and physical gelation and synthesis monitored with UV-Vis spectrophotometer for the

Introduction:

Adsorption/desorption studies are useful for generating essential information on the mobility of chemicals and their distribution in the soil, water and air compartments of our biosphere (OECD, 2000). They can be used in the

Surface Plasmon Resonance (SPR) of silver nanoparticles. Product CVNPS were characterized by UV-Visible Spectrophotometry, Fourier Transform- Infrared (FT-IR), Field Emission Scanning Electron Microscopy (FESEM), High Resolution Transmission Electron Microscopy(HRTEM), Energy Dispersive X-Ray (EDX), Selected Area Electron Diffraction (SAED), Powder X-Ray Diffractometry (PXRD), Differential Scanning Calorimetry (DSC) and Thermogravimetry Analysis (TGA). The SPR of CVNPs was 403nm. The morphology was spherical, monodisperse and average size range of 11nm. EDX, SAED and PXRD confirmed the silver (Ag) presence with the revelation of reflections of silver nanoparticles indexed as (111), (200), (220) and (311) with the corresponding 2θ values of 38.4° , 44.4° , 64.1° and 77.7° respectively. The adsorption of dichlorvos onto CVNPs has been found to depend on initial concentration and contact time. The experiments were carried out at pH of 6.5. Equilibrium data fitted well with the Langmuir and Freundlich models with values of R^2 of Langmuir better with a maximum adsorption capacity of 33.33 mg/l. The experiments showed that the highest adsorption rate was 92% for dichlorvos (VOS). Desorption pattern showed hysteresis, while sorbed dichlorvos depicted slow release, thus making CVNPs suitable matrix for slow release formulation of pesticides.

Keywords: Kinetics, Starch nanoparticles, adsorption-desorption dichlorvos

prediction or estimation, for example, of the availability of a chemical for degradation, transformation and uptake by organisms, leaching through the soil profile and run-off from land surfaces into natural waters (Bajeer *et al*, 2012, Bakhtiary *et al*, 2013).). Adsorption data can also be used for comparative and modelling purposes (OECD, 2000).

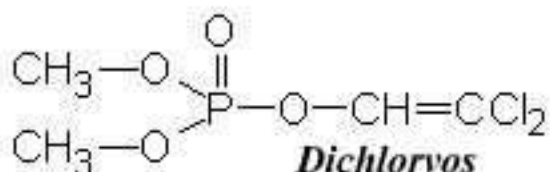
Sorption which is one of the most important processes that determines their distribution in the soil/water environment, generally describes the process of a pesticide partitioning between water solution and soil (Bajeer et al, 2012). Sorption also determines availability of pesticides in the soil solution that governs the amount of pesticide that is available for uptake by plants and the effectiveness of pesticides (Bajeer et al, 2012).

Recently, various sorbents have been used in studies to remove, dyes, metal ions, organic compounds, pesticides and the heavy metals from water and waste water via sorption (Rachkovskaya, *et al*, 2016, Alishavandi *et al*, 2013, Vasileva *et al*, 2013). These materials have some comparative advantages in contrast to common sorbent materials. In the last decade, researches have prepared new Ag sorbents using various materials by miscellaneous methods (Rachkovskaya *et al*, 2016, Alishavandi *et al*, 2013).

Metallic nanoparticles like silver nanoparticles, have found uses in many applications in different fields, such as in catalysis, medicine, photonics, and electronics. The synthesis of metal nanoparticles has been widely discussed in literature due to their unique physical and chemical properties, which have many potential applications (Sood et al, 2017 and Nagajyoity *et al*, 2011, Gao *et al* 2011 & Daroudi *et al*, 2011). The intrinsic properties of metal nanoparticle are mainly determined by its size, shape, composition, crystallinity, and structure. They are different properties from their bulk materials and have small size with large surface area (Gao *et al* 2011).

Starch silver nanoparticles (St-AgNPs), is a structurally homogenous material of very high surface area, their ordered structure, high aspect ratio, ultra-light weight, high mechanical strength offers a very high adsorption capacity and may be widely used as an adsorbent in many industrial processes (Alishavandi et al, 2013).

Dichlorvos, O-2,2-dichlorovinyl-O,O-dimethyl phosphate (DDVP), is a chlorinated organophosphate insecticide that is extensively used in many countries for controlling insect pests on agricultural, commercial, domestic, and industrial sites. Compared to other pesticides, dichlorvos is generally preferred because of its cost-effectiveness and wide range of bioactivity (Liu et al, 2009)



It has been reported that the performance of pesticide loaded organo-clays as a slow-release formulations strongly depends on the desorption pattern of the retained pesticides (Bakhtiary et al 2013). If the pesticide partly reversibly bound to the matrix, desorption will occur with subsequent irrigation or rainfall and the active ingredient gradually release to the soil solution (Bakhtiary et al 2013). In this paper, the feasibility of applying St-AgNPs as low-cost adsorbent /desorbent from aqueous solution of dichlorvos insecticide over different concentration will be studied and the adsorption data tested for a number of isotherm equations.

Experimental section

Materials

Dichlorvos was obtained from AgroChina (China). Silver nitrate (AgNO₃) and glucose was purchased from Finlab Abuja, Nigeria. Starch was isolated from cassava tubers purchased from Karimo Market in Abuja, Nigeria. Distilled water was used throughout the experiments.

Preparation of stock solution of the insecticide

Stock solutions of the insecticides were prepared by dissolving them in acetone at various concentrations. The UV-Vis spectrophotometer was used for analysis (Kakavendi *et al*, 2014), and construction of a calibration curve at its maximum wavelength for the absorbance values of the solutions were measured corresponding to the various solute concentrations depending on the Beer's law ($A = \epsilon bc$). The concentration of free (unbound) insecticide in the supernatant was determined from the calibration curve, and the amount of dichlorvos bound on the unit volume of absorbent was estimated by difference.

Synthesis of starch Silver nanoparticle (ST-AgNP)

The aqueous solution of molar silver nitrate (AgNO_3) and glucose was used for the synthesis of silver nanoparticles. According to slightly modified methods of, Gao *et al.*, (2011) and Ramakrishna *et al.*, (2012). One percent (1%) w/v dispersion of the cassava (CV) starch separately in distilled water was stirred for 20 minutes in a loosely covered bottle at elevated temperature (50 °C) respectively. Then, 1ml of 0.06M solution of AgNO_3 was added and the transparent solution was stirred for another 5mins, followed by addition of 3ml of 0.2M glucose solution and stirred for 10mins after which, the complex was heated (Corning hot plate/stirrer, PC- 351) for 3hours at 80-90°C.

The complex was allowed to cool and centrifuged at 11,000rpm for 20minutes using Eppendorf centrifuge 5417R. The resultant nanoparticle was oven-dried at 40°C for 24hours, ground to powder, stored in a closed dark container devoid of sunlight. Blank was prepared using the same procedure excluding the addition of silver nitrate and glucose solutions respectively.

The percentage yield W/W was calculated by the weight of dried recovered nanoparticles (W_1) and the sum of the initial starting weight (W_0) by the formula according to Ihegwuagu et al, (2009);

$$\text{Yield (\%)} = \frac{W_1}{W_0} \times 100 \quad \dots\dots\dots 2.1$$

Swelling Capacity of ST-AgNP

This was carried out according to Bajpai et al, 2013. Swelling of native starch and starch silver nanoparticles was studied by a conventional gravimetric procedure. In a typical experiment, 20mg of both nanoparticles and native starch were allowed to swell in a definite volume (10 mL) of phosphate buffer (pH 6.5) taken in a pre-weighed graduated glass tube and weighed after a definite period by removing excess phosphate buffer with the help of a suction apparatus. The swelling of nanoparticles was monitored continuously from 1 hour up to 24hours after which no weight gain of swollen nanoparticles was recorded which clearly indicated the arrival of equilibrium swelling conditions. The amount of water imbibed by the nanoparticles was calculated by the following equation;

$$\text{Swelling ratio} = \frac{W_t}{W_0} \quad \dots\dots\dots 2.2$$

Where W_0 and W_t are the weight of dry and swollen nanoparticles at 0 and time t, respectively. A plot of the observation was made.

Characterization of starch silver nanoparticles

UV-Vis Spectral analysis: The synthesized ST-AgNPs were confirmed by monitoring aqueous component's absorption maxima by UV-Vis spectrophotometer at the wavelength of 300-800 nm on UV- Agilent, Model 8453 Chemstation software spectrophotometer.

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

Morphological analysis: Morphological analysis was done using a: High Resolution Transmission Electron Microscope (HR-TEM) (FEI TECNAI 02) having software TECNAI G². 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. Thin films of the sample were prepared on a carbon coated copper grid by just dropping a very small amount of the grid, extra solution was removed using a blotting paper and then the films on the HR-TEM grid were allowed to dry by putting it under mercury lamp for 5 min. The particle size was calculated with the Image J software and histogram of particle size distribution plotted with Microsoft excels 2010 software.

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

Structural analysis: Powder X-ray Diffraction (PXRD)

The synthesized ST-AgNPs was structurally analysed using the Diffractometer, D8 Advance (by BRUKER AXS, Germany) and the XRD pattern analysed according to JCPDs patterns.

The X-ray diffraction (XRD) pattern was measured by drop coated films of AgNO_3 on glass plate and employed with characteristic radiation in the range of 200 to 900 at a scan rate of 0.050/min with the time constant of 2 s, $\text{CuK}\alpha$ radiation and amplitude wave $\lambda = 1.5418 \text{ \AA}$ working with a 40 kV voltage and 30 mA current. The full–width at half–maximum (FWHM) from three different peaks were

used in Scherer's equation to determine the average crystallite size of the nanoparticles.

Thermal analysis: Differential scanning calorimetric (DSC)

The analyses of the silver nanoparticles, nanoinsecticides formulations and carrier had their possible interactions and thermal stability evaluated with the differential scanning calorimetry. The Instrument model used was DSC Q2000 V24.1 Build 122 Module DSC Standard Cell RC. Samples (7.0700 mg) were heated under nitrogen (25.0 ml/min) atmosphere on aluminium over the temperature range of 5 and 300°C. Thermal data analyses of DSC thermograms were conducted using Origin Lab, software (Version 6.1).

Thermogravimetric Analysis (TGA)

Thermal characterization of the materials was carried out by thermogravimetric analysis (TGA) on 30 mg samples by heating from 50 to 800 °C at 20 °C /min, under nitrogen or air flow (100 ml/min) using a TA Instruments thermo balance TGA Q500 V20.13 Build 39. TMAX is defined as the temperature of maximum rate of weight loss.

Adsorption -desorption

The Batch equilibrium Method

The insecticide adsorption- desorption procedure was performed using batch equilibrium technique according to Nnamonu, (2011) and Bakhitary *et al* (2013). 10 mg silver nanoparticles (as well as control) adsorbent samples were added into conical centrifuge tubes with 10 mL of aqueous solution containing different insecticidal concentrations (ranging from 0.0001- 0.1M) in buffer of pH 6.5 in duplicate. The mixtures were shaken at ambient temperature of 20 ± 0.5°C and constant agitation using orbital shaker at speed 8rpm for 24 hours. The mixtures were then centrifuged at 3500 rpm for 20

minutes. Insecticide solutions (blank) were also investigated without the sorbents and they served as controls. The pH was noted and residual insecticide concentration was finally determined spectrophotometrically using an Agilent 8453 UV-VIS Spectrometer system at their various wavelengths of absorption.

The amount of insecticides adsorbed by the sorbents was calculated from the difference between the initial and final solution concentrations.

Using the following mass balance equation:

$$Q_e = \frac{V(C_i - C_e)}{M} \dots\dots\dots 2.3$$

Where Q_e is the insecticide (VOS) adsorbed (mg/L), C_i and C_e are the initial and equilibrium concentrations of VOS (mg/L), respectively, M is the mass of adsorbent (mg), and V is the volume of the solution (L). The percentage removal of atrazine was calculated by the following equation

$$\text{Percentage removal} = \frac{(C_i - C_e)}{C_i} \times 100 \dots\dots\dots 2.4$$

where C_i and C_e are initial and equilibrium concentrations (mg/g) of atrazine solution, respectively.

Two common adsorption isotherm models (Langmuir and Freundlich) were used to describe the relation between adsorbed and soluble insecticides at constant temperature.

Langmuir isotherm which assumes adsorption is monolayer in nature was applied to quantify the maximum amount and the affinity of dichlorvos adsorption on the sorbents. This isotherm has the form of:

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \dots\dots\dots 2.4.1)$$

where Q_e is the insecticide adsorbed at equilibrium (mg/L), C_e is the equilibrium insecticide concentration (mmol/L), Q_{\max} is the adsorption maximum (mg/L), and K_L is the Langmuir coefficient, showing adsorption affinity (L/ mg). A plot of C_e/Q_e versus C_e is made and slope of this plot gives $1/ Q_{\max}$ and intercept $1/ Q_{\max} K_L$. From where Q_{\max} and K_L were calculated.

In order to determine whether the adsorption process by the starch silver nanoparticles is favourable, a dimensionless constant called separation factor (R_L) was calculated from the Langmuir constant as follows (Bakhtiary *et al*, 2013).

$$R_L = \frac{1}{1 + K_L C_0} \dots\dots\dots 2.4.2)$$

Based on the R_L value, both the isotherm shape and the adsorption mechanism can be predicted. The smaller R_L value indicates the more favourable adsorption. The value of R_L indicates either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible adsorption ($R_L = 0$)

Freundlich model is expressed by the following equation:

$$Q_e = K_F C_e^{1/n} \dots\dots\dots 2.4.3$$

Where K_F is the Freundlich partition constant and n is a physical factor related to adsorption mode and surface heterogeneity. Q_e and C_e were described before. The Freundlich isotherm has been derived by assuming an exponentially decaying adsorption site energy distribution (Bakhtiary *et al*, 2013). $1 \leq n \leq 10$ represents the favourability of adsorption process (Bajeer *et al*, 2012).

A plot of $\log C_e$ against $\log Q_e$ gives a slope which is equal to $1/n$ and an intercept equal to $\log K_F$.

The Insecticide desorption experiment

Desorption of insecticides from the silver nanoparticles and control samples were measured immediately after adsorption at the highest initial concentration using successive dilution method according to Bakytary *et al.*, (2013). After shaking of the insecticide – sorbent mixtures at ambient temperature ($20 \pm 0.5^\circ\text{C}$) for 24 hours, the supernatants were separated by centrifugation at 3500 rpm for 20 min. Then, 7mL of the supernatant was removed to determine individual insecticide concentration, and replaced with 7 mL of buffer (pH 6.5). This was shaken for 2hours, centrifuged at 3500rpm for 20mins. This desorption cycle was repeated four times each time in duplicate, pH was noted and desorption isotherms were prepared by plotting the insecticide that remained on the experimental samples after each desorption cycle vs. the corresponding equilibrium insecticide concentrations in solution respectively.

The percent desorption (%) = $\frac{\text{Amount of dichlorvos liberated by water}}{\text{Amount of dichlorvos adsorbed on adsorbent}}$

X 1003.1

Amount of dichlorvos adsorbed on adsorbent

Data Analysis

Data was analysed for the sorption data with origin lab (version 6.00) for Windows, Microsoft excel Software and SPSS 21. Determination coefficients (R^2) values were used to evaluate the goodness of fit of the isotherm equations to the data.

RESULTS AND DISCUSSION



Figure 1: The step-wise synthesis of starch silver nanoparticles where a, is the starch- AgNO_3 -glucose complex, b-e the steps and f (brown) the end product.

Characterization of ST-AgNPs

UV-VIS Spectrophotometric analysis

The UV-VIS spectrophotometric plots of both CVNPS and MZNPS are presented in Figure 1. The Formation of Ag nanoparticles in the colloidal solution was monitored from their absorption spectra as the small noble metal particles reveal absorption band in the UV-Vis spectral region due to surface Plasmon resonance (SPR) (Alishavandi et al, 2013). It was found at 403nm. The reduction of Ag^+ ions with glucose in the presence of starch aqueous solution at leads to the formation of Ag nanoparticles (Ihegwuagu et al, 2014).

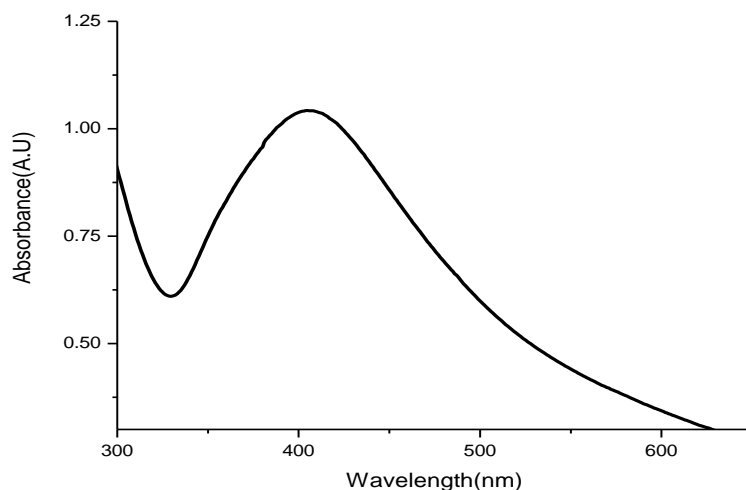


Figure2: The UV- Vis Spectral of cassava silver nanoparticle (CVAgNPs)

Morphology Studies

High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM was used to study the morphology of the synthesized silver nanoparticles. The images at different resolutions is shown in Figure 3. Some nanoparticles appear to lay on each though those beneath can still be seen. The results differ from the native that had no black silver sphere on the particles.

The HRTEM was coupled with Selected Area Electron Diffraction (SAED). The images pattern of the AgNPs obtained are shown in Figure 3 sub sets. They are characterized with ring-like bright dots.

Energy Dispersive X-ray (EDX) Analysis

The Energy Dispersive X-ray (EDX) was also coupled with HRTEM. The EDX analysis signal as shown in Figure 4. It revealed the elemental composition of the AgNPs, depicting silver as the major element present on both matrices. The typical optical absorption

band silver metallic peak found within the 3Kev, confirms nanosilver on matrix due to Surface Plasmon Resonance. This silver peak was absent on the control(native) (Figure 4).The other signals showing on the spectrum include carbon and oxygen due to the presence of starch in the nanoparticles and copper as a result of the copper grid on which the nanoparticles were immobilized during HRTEM analysis (Kumar *et al.*, 2011).

Fourier Transform - Infra-Red (FT-IR) Analysis

The FTIR spectra of the starch silver nanoparticles were recorded in order to identify the functional groups of glucose and starch involved in the reduction and capping/stabilization of the synthesized nanoparticles

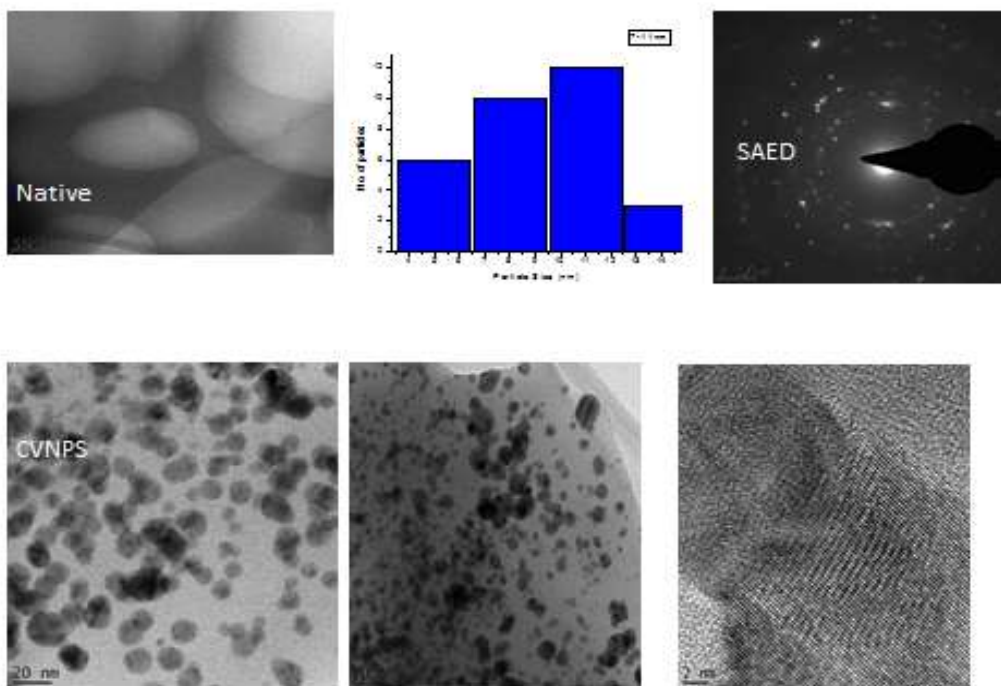


Figure 3: HRTEM of CVNPS showing spherical monodisperse particles, size distribution as well as the bright crystal dots in SAED image.

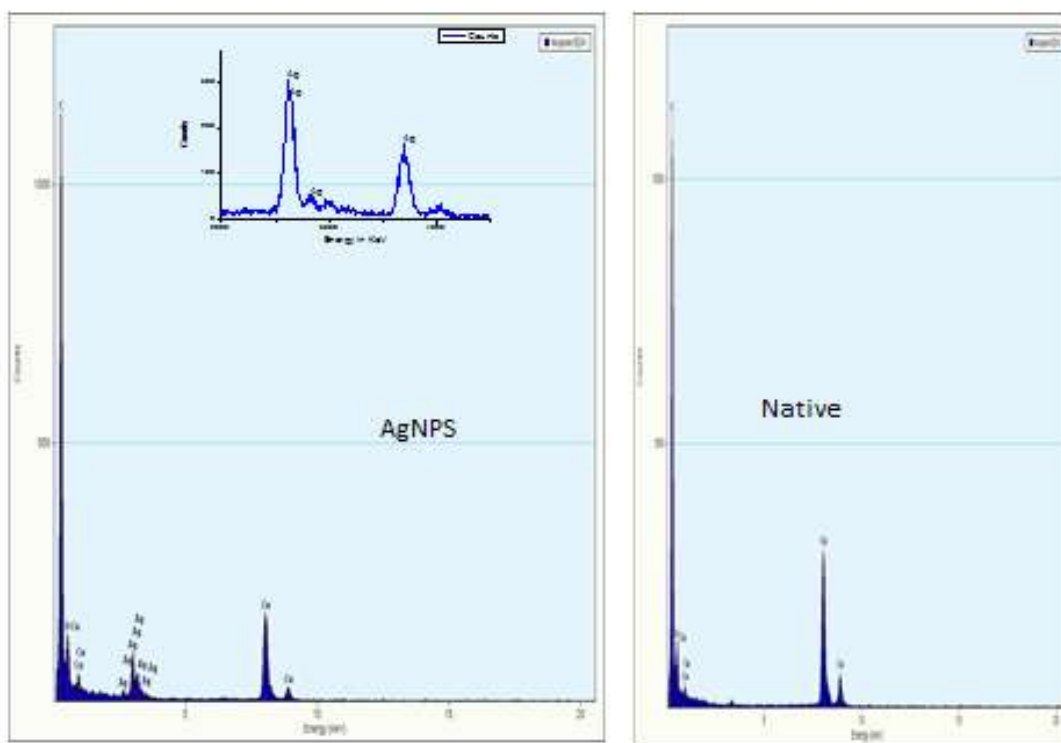


Figure 4: EDX spectrum of AgNPS showing silver peaks

Powder X-Ray Diffraction Studies

The X-ray diffraction pattern obtained for the silver nanoparticles synthesized by chemical reduction method is shown in Figure 7.

Thermogravimetry Analysis (TGA)

TGA was also used to provide further understanding of the thermal behaviour and the decomposition of the sample. The result is presented in Figure 8. While CVNPS lost absorbed water at 118 °C, its degradation started to at 242 °C and ended at 343 °C, MZNPs lost moisture earlier at 106 °C and began degrading at 262 °C and completed degradation at 318 °C.

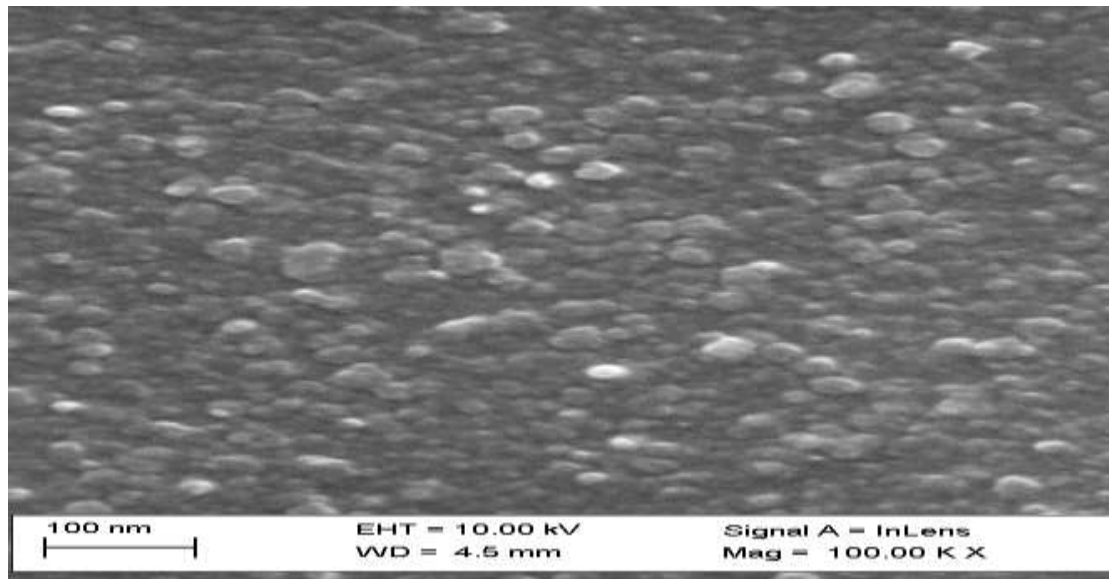


Figure 5: shows the FESEM of the synthesized AgNPs.

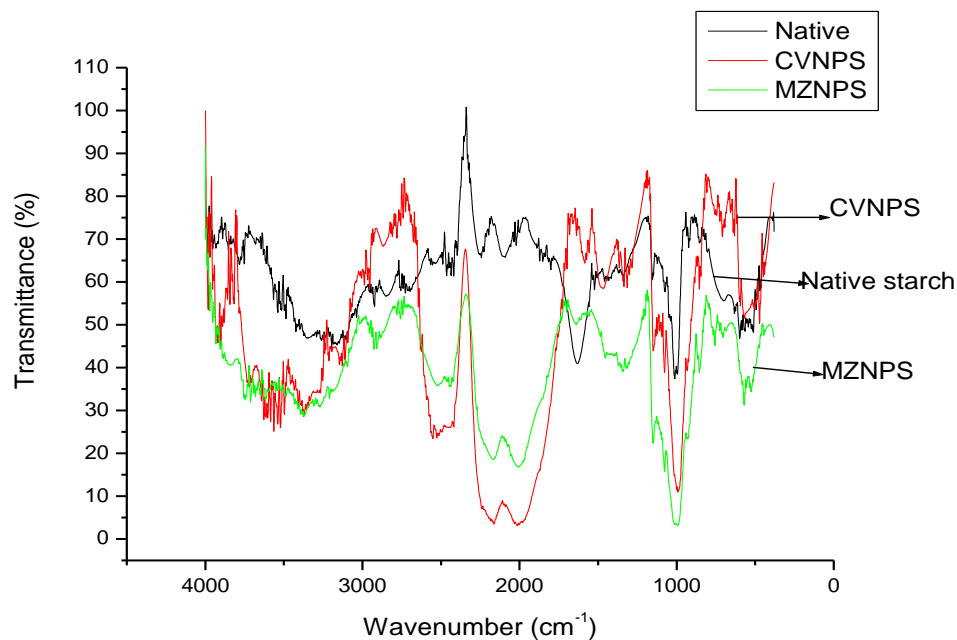


Figure 6: FT-IR of Native starch, CVNPS & MZNPS nanoparticles

Table 1: FT-IR Functional Group Analysis

Vibrational Assignment/Functional group	Observed wave number (cm ⁻¹) in CVNPS	Observed wave number(cm ⁻¹) in Native starch
OH	3376	3347
CH ₃	2930	2925
C=O	1591	1631
Peak maybe Gluconic	1346	1347
C-O- stretching	1001	3347

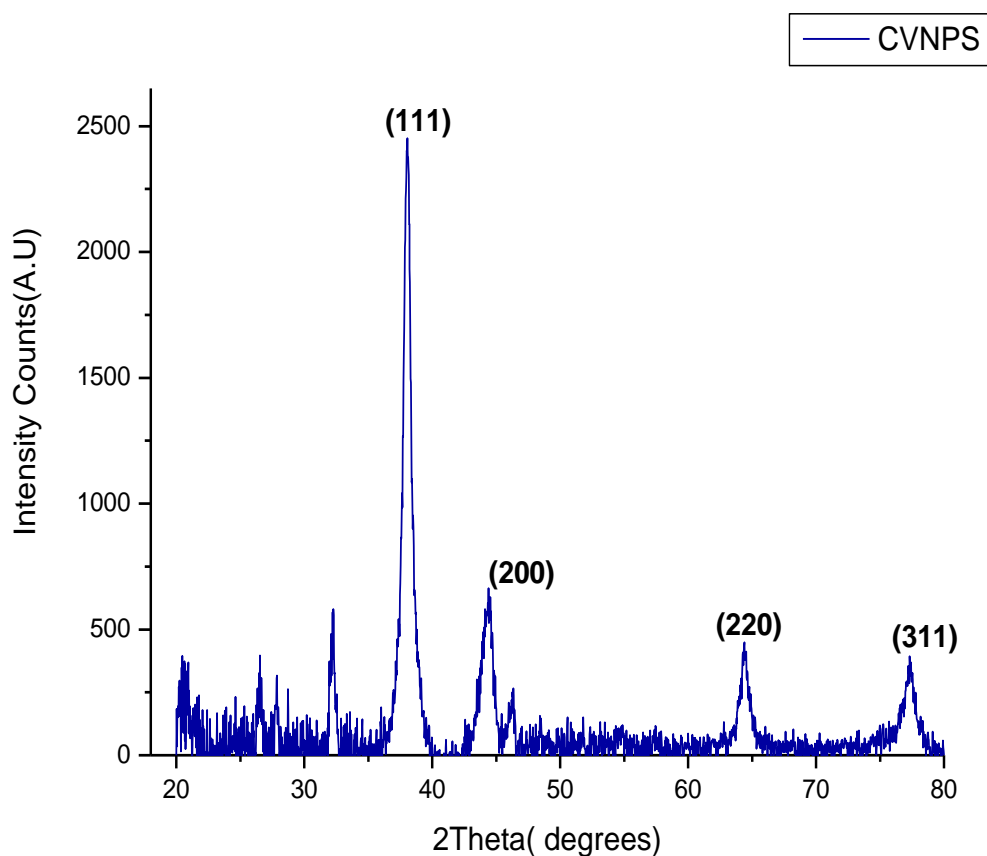


Figure 7: PXRD pattern of CVNPS revealing all Bragg reflections

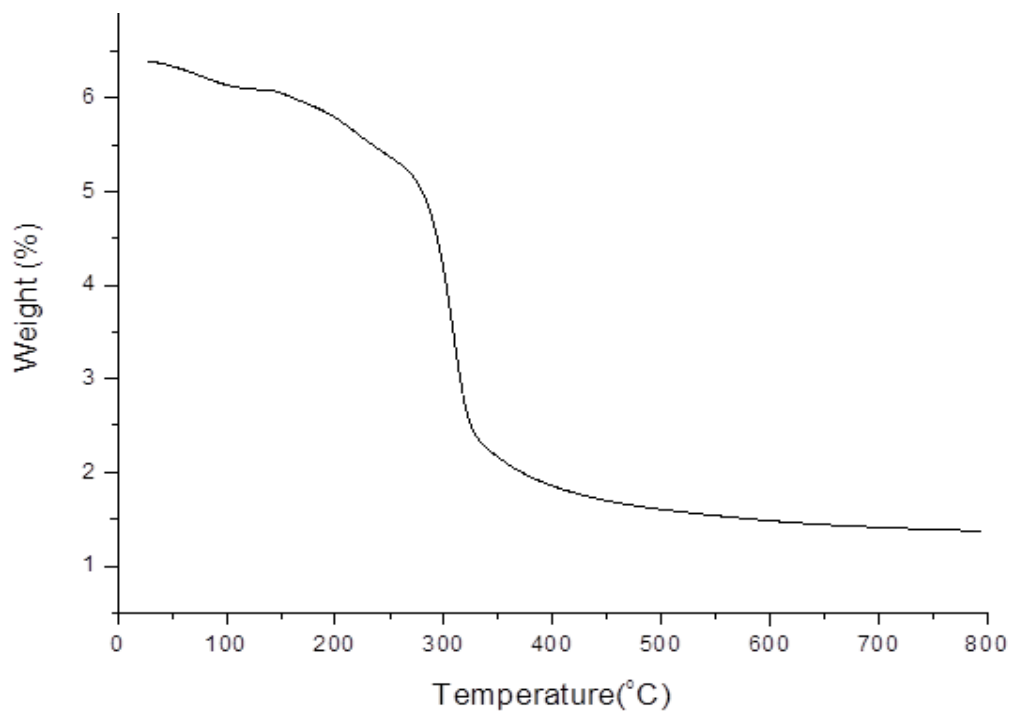


Figure 8: Thermogravimetry pattern of the synthesized nanoparticles

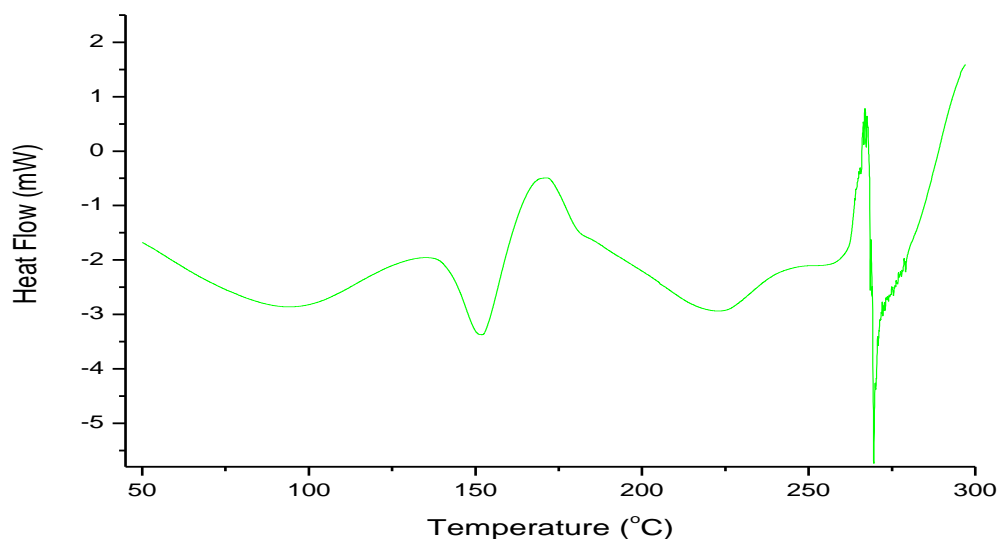


Figure 9: DSC of AgNPS

Adsorption- Desorption

Adsorption isotherms are mathematical models that describe the distribution of adsorbate species between liquid and adsorbent, based on a set of assumptions that are mainly related to the heterogeneity/homogeneity of the adsorbent, the type of coverage and possibility of interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms such as the Langmuir and Freundlich isotherms. These isotherms relate adsorbate uptake per unit weight of adsorbent (q_e) to the equilibrium adsorbate concentration in the bulk fluid phase C_e (Kumar, *et al.*, 2010). The results of the batch method adsorption experiment conducted in this study were fitted with the well-known Langmuir and Freundlich adsorption models. The Langmuir (Q_{max} is the adsorption maximum (mg/L), and K_L is the Langmuir coefficient, showing adsorption affinity (L/mg)) and Freundlich (where K_F is the Freundlich partition constant and n is a physical factor related to adsorption mode and surface heterogeneity) adsorption constants with the correlation coefficients of dichlorvos is presented in Table 2. The correlation coefficients showed that the adsorption process could be described by both Langmuir and Freundlich models. Their plots were shown in Figures 10 (a-d)

Looking at Table 2, it could be seen that the Langmuir K_L constant for nano dichlorvos was greater than those of native dichlorvos CVNPsVOS (0.0019) > NativeCVVOS (0.0003) > No sorbent blank (0.0000046).

In the Freundlich analysis, the K_F showed a reverse order Native CVVOS (1.1) > CVNPsVOS (0.7) > No sorbent blank (0.01). All showed favourability. The R^2 values ranged from 0.7955 to 0.9968 for both Langmuir and Freundlich (Table 2).

Table 2: Isothermal Adsorption Parameters of Dichlorvos (VOS) and Control.

Sorbent Sample:	Langmuir			Freundlich		
	K_L (mg/l)	Q_{max}	R^2	K_F	n	R^2
CVNPVOS	0.0019	3333.3	0.9938	1.54	0.80	0.9092
NativeCVVOS	0.0003	5000	0.9918	1.86	0.62	0.8913
No sorbent	4.5E-6	166,667	0.8521	0.38	2.6	0.7955

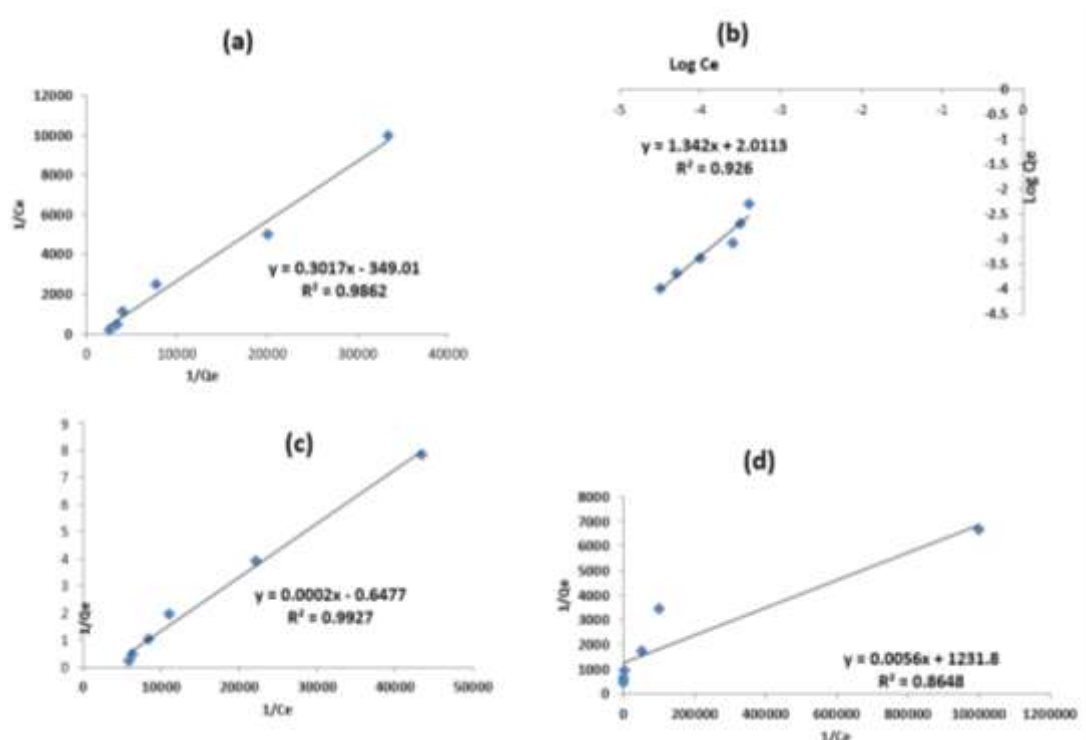


Figure 10: The Langmuir (a), and Freundlich (b) for CVNPVOS as well as Langmuir (c), (d) for native CVOS and no sorbent sample

isotherm models for the adsorption of dichlorvos (VOS) on ST-AgNP.

Adsorption Pattern of DDVP

The effect of initial concentration on dichlorvos adsorption using starch AgNPs are shown in Figures 11, with error bars ($n = 6$). This study was conducted at $\text{pH } 6.5 \pm 0.5$ at ambient temperature. These figures depicts that percent adsorption of CVNPVOS was high (92%) at lower equilibrium concentration of dichlorvos (VOS) and vice-versa. The percentage removal decreases with an increase at the initial concentration. This can be explained by the fact that the adsorbent, starch- silver nanoparticles (CVNPVOS) had limited active sites, (since its dosage was same for all the experiment) which would have become saturated above a certain concentration. This is in agreement with Biakhtiary et al, (2013). Almost the same trend was observed with the native starch adsorbent without silver but the blank (no sorbent).

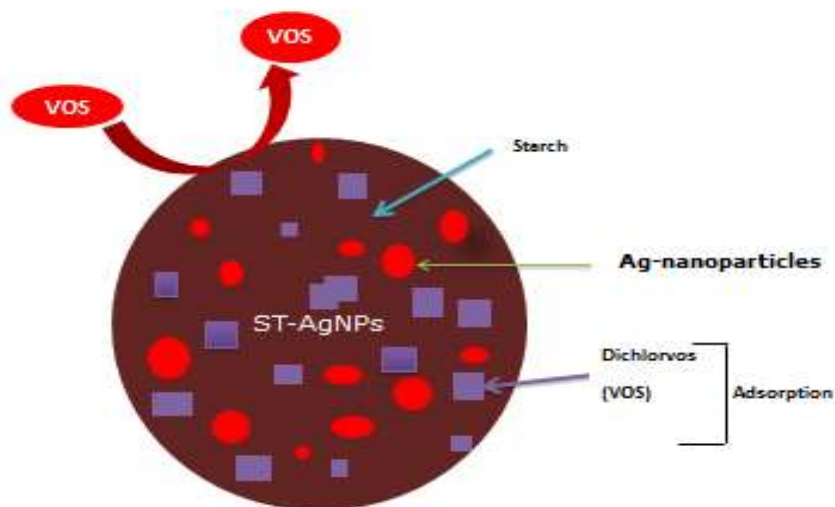


Figure 11: schematic adsorption steps for dichlorvos

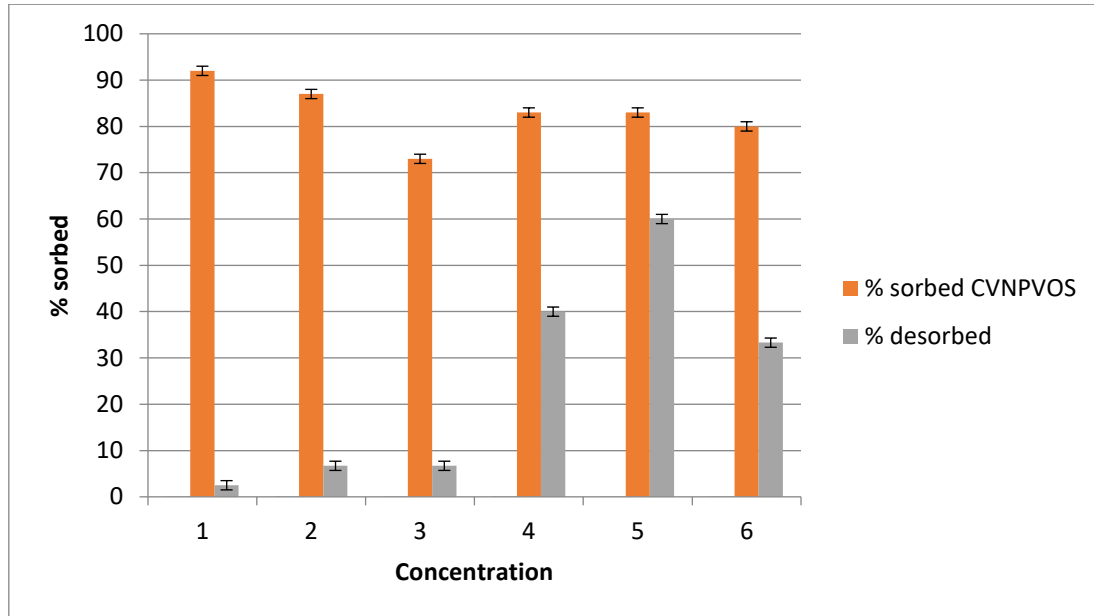


Figure 12: Sorption -desorption of dichlorvos on starch silver nanoparticles

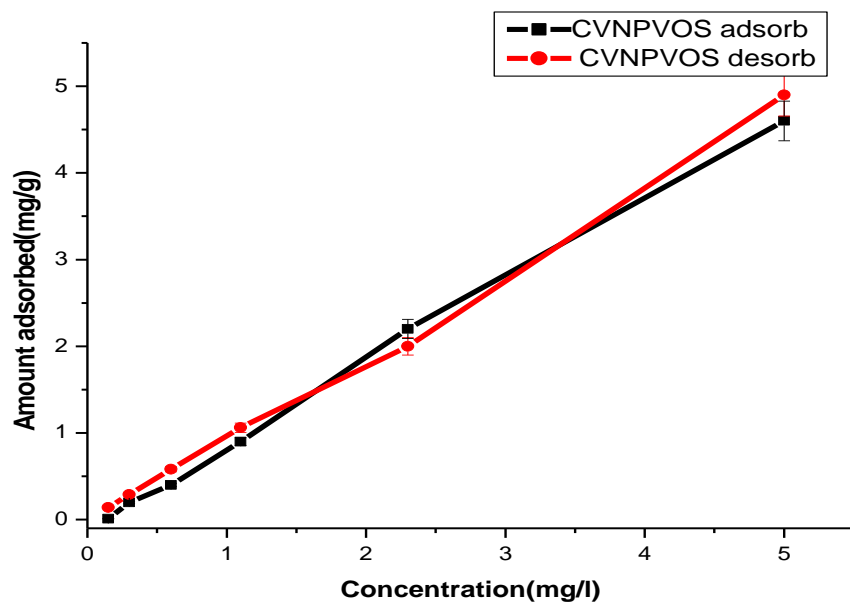


Figure 13: Dichlorvos (VOS) sorption-desorption isotherms on CVNP Nanoparticles

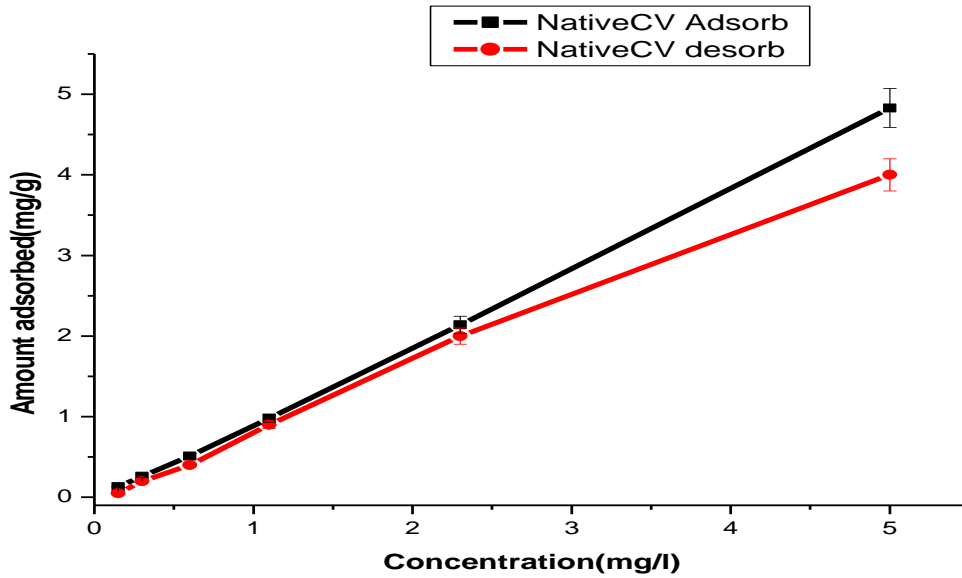


Figure 14: Dichlorvos (VOS) sorption-desorption isotherms on NativeCVOS

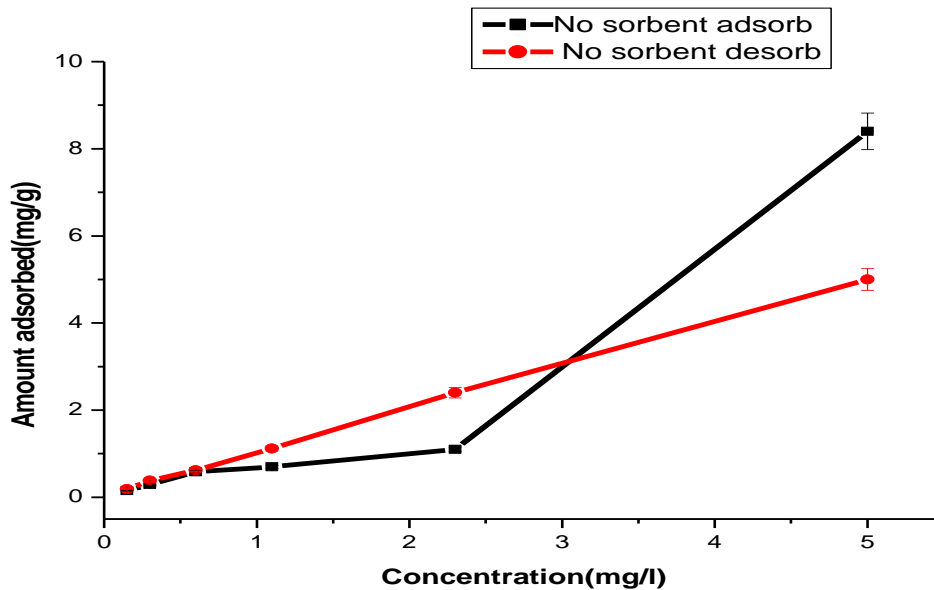


Figure 15: Dichlorvos (VOS) sorption-desorption isotherms on No sorbent (blank)

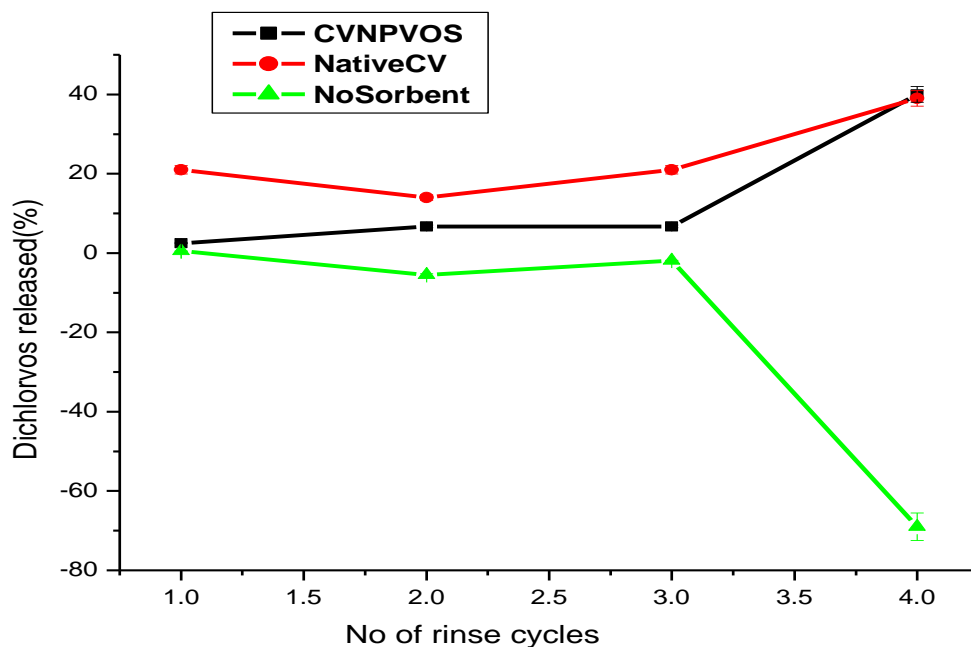


Figure 16: Dichlorvos (VOS) released after rinse cycles

Conclusion

In this work, starch was proven to be an effective stabilizer for (AgNP) nanoparticles. The starch stabilized nanoparticles demonstrated comparable high removal efficiency towards Dichlorvos at ambient temperature without the need of pH adjustment than the native starch. Starch as a low-cost and green stabilizer could be a suitable candidate to enhance silver nanoparticles absorptivity for dichlorvos insecticide contamination from aqueous solutions and may potentially reduce leaching if used in slow release formulations of pesticides. Hence, affordable green processes must be developed to ensure complete mineralization of pollutants (Saadati et al., 2016)

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