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Controlled Release Formulation of Dichlorvos and Diazinon Using Biocompactible Starch For Agro-Environment Sustanability

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Abstract
The study was carried out with the aim of encapsulating suitable and sustainable controlled release micro formulation of dichlorvos and diazinon; organophosphate pollutant used as a pesticide for agriculture in Nigeria with low cost adsorption of the insecticides; dichlorvos and diazinon matrix. The maximum absorbance of dichlorvos derivative and diazinon were measured at the wavelength of 401 nm and 265 nm respectively. Langmuir and Freundlich adsorption isotherms fitted the adsorption data generated at pH 4.0, 7.0, 9.0 and 25^0C for the different surfaces. Langmuir and Freundlich adsorption isotherm were used to model the adsorption process. Controlled release formulations (CRFs) were synthesized from sodium alginate-modified starch matrix and cross-linked with 0.25M $CaCl_2$ solution. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and powder X-Ray diffractometry (PXRD), were used to characterize the CRFs.

Keywords*: adsorption, starch, CRFs, dichlorvos and diazinon*

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I. Introduction

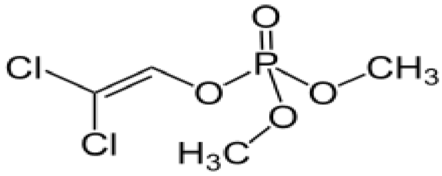
The vast majority of the world's hungry people live in developing countries where 12.9% of the population is undernourished [7]. The economy of third world countries is centred mainly on agriculture, whose output has continued to lag behind the world's food demands [12]. Pesticide formulation which are mostly use by farmers, reduce labour costs and energy consumption and in so doing, increase labour efficiency and food production[2]. Most of the commonly used pesticides are classified, using empirical toxicological data, as endocrine disruptors, carcinogens and nerve toxins. Parenthetically, interactive drawback associated with conventional formulations of pesticides presently in use, is the release of much of their active ingredients into the immediate environment, which results in significant loss of the active ingredient in the field via the dissipation pathways of hydrolysis, volatilization, evaporation, and leaching. A consequence of this loss is their repeated and often excessive application in farm plots or field situation. It has been estimated that 90% of applied pesticides do not reach their target areas at the right time and in efficacious quantities [18]. Thus, in addition to toxicity problems, conventional methods of pesticide application impact negatively on the economics of food and fibre production.

The search for more efficient methods and processes which afford higher yields and a better quality that require less time, money, methods and processes, and do not pose a threat to the environment, has received an impetus with the recent adoption of the Sustainable Development Goals (SDGs) as the current global development paradigm for the period 2015 - 2030 [14,33]. This formulation is a recent strategy, borrowed from the drug industry, that releases the chemicals slowly, in a controlled and sustained manner and are such called slow or controlled release formulations (SRFs or CRFs) [28,4]. The formulation and optimization of biodegradable, biocompatible pesticide-laden matrix as delivery systems provide answers to the problems associated with pesticide use in food and fibre production as outlined above.

Dichlorvos and diazinon as shown in Fig. 1are broad spectra organophosphateinsecticide. They are use in agriculture and horticulture for the control of insects in crops, ornamentals, lawns, fruit and vegetables and as pesticides in homes and public buildings. As a result of their wide usage and application by conventional methods, its residues are usually found in food crops, natural water systems and in soils [34].Therefore, there is need forCRFs of the both insecticide typeswhich are cleaner and safer for the user, having minimal impact on the environment and are applied at the lowest dose rate [20,5]

This research is set out to encapsulate dichlorvos and diazinon, the active ingredient (a.i.) into starch cross-linked with sodium alginate. Starch attracts considerable attention as a polymeric material for CR because, apart from it being renewable, abundant, and inexpensive, it can be easily modified chemically, physically and biologically into low molecular weight or high molecular weight compounds for specific applications [6,21]. It is a non toxic, biodegradable and biocompatible [30] matrix, whose CRFs enhances easy application by farmers and minimise direct contact with the environment.

a



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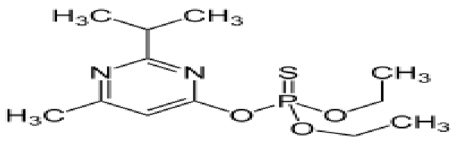


Fig. 1: (a) dichlorvos and (b) diazinon

II. Materials and Methods

2.1. Materials

Dichlorvos (DDPV), diazinon both are technical grades and sodium alginate were acquired from Zayo Sigma Jos, Nigeria. Phthalate buffer pH 4.0 solution, potassium dihydrogen phosphate, acetone, sodium hydroxide, glacial acetic acid, calcium chloride, sodium chloride, ninhydrin, dimethyl sulphide (DMSO) were all suppliedby NAFDAC Zonal Laboratory, Agulu, Nigeria.andchemicals were used as received.

2.2 Preparation of stock solutions for calibration experiments

2.2.1 *Dichlorvos and diazinon*

A stock solution of dichlorvos and diazinon of 1000 μg/ml was prepared by dissolving 0.045 mmol of dichlorvos in acetone and made up to 100 ml mark with milli-Q water. The volumes of the stock solution were measured into 10 ml volumetric flasks using an Eppendorf pipette to obtain solutions whose corresponding concentrations range between 10.0 - 30.0 µg/ml, after making up to the mark with milli-Q water.

2.2.2 *Preparation of ninhydrin-dichlorvos reagent for calibration curve*

1 ml dichlorvos sample solution was added into 2 ml of the ninhydrin reagent in a plastic screw-capped bottle. The ninhydrin reagent was prepared by adding 30 ml of DMSO into a conical flask containing 1.4 mmolninhydrin with stirring, 0.043 ascorbic acid was added with further stirring for another 3 minutes to ensure complete dissolution [19].

2.3 Preparation of controlled release formulations(CRFS)

A 3% (w/w) aqueous dispersion containing of sodium alginate in 100 ml of water, 2% (w/v) of the pesticide (0.02 g in 1ml of acetone) and 15% (w/w) of each matrix was vigorously stirred for 10 minutes. The CR beads were formed by dripping the slurry from a 500 ml syringe from a height of approximately 20 cm into excess 200 ml gelling solution made up of 0.25M $CaCl_2{\cdot}2H_2O$ in 2% v/v acetic acid at 25^0C. The beads, which were allowed to set for 25 minutes, were filtered using a funnel, washed twice with Milli-Q water and air-dried. Blank beads were prepared in the same way but without any active ingredient.

2.4 characteristics of the insecticides-loaded beadsusingfourier transforms infra-red (FTIR) and powder x-ray diffraction (PXRD)

TheFTIR spectra were obtained for the pulverized samples of blank starch anda.i-incorporated CRFs, using a Thermo-nicolet 380IR, USA FTIR spectrophotometer. The samples were scanned within the range 400-4000 cm^{-1} at a resolution of 2 cm^{-1}. In PXRD analysis,the prepared insecticidal controlled release starch formulations of dichlorvos and diazinon were structurally analyzed using the diffractometer, (INEL Equinox 1000g/N USA).The samples were first sieved onto the surface of a silicon disc pre-coated with petroleum jelly, and then scanned from 0-140^0 (2θ)at the speed of 5/min.

2.5. Scanning electron microscopy (SEM)

SEM images of the CRFsamples were recorded using a Tecnai 920, USA scanning electron microscope, equipped with energy dispersive analysis of X-rays (EDAX) at the required magnification. The acceleration voltage used for the SEM instrument was 10 keV with the secondary electron image (SEI) as a detector.

2.6. Studies of adsorption equilibria

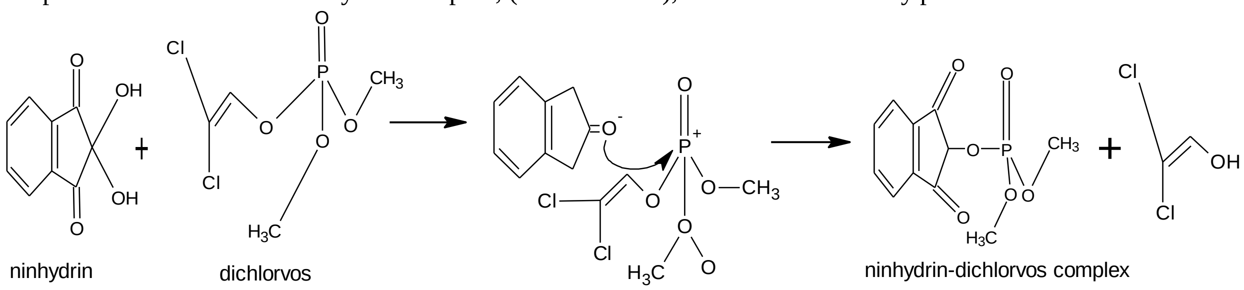
Adsorption equilibrium studies involving the pesticides of interest were undertaken, using the batch equilibration method [26, 24]. 10 ml of the buffer solutions (pH 4, 7 and 9) and 40 ml of diazinon and dichlorvos solutions were introduced into a Teflon bottle containing 250 mg of the adsorbent, respectively. The samples were thoroughly shaken on a mechanical shaker for 1 hour at the temperature 25°C. The suspension was subsequently centrifuged (Megafuge, Heraeus) at 4500 rpm for 10 minutes. Five ml of the supernatant was withdrawn for UV-Vis spectrophotometry (Shimadzu Japan) analysis of the active ingredient at the wavelength of 401 and 264 nm for dichlorvos and diazinon, respectively. Each experiment was duplicated. Pesticide solutions in buffer without the adsorbent were also treated in similar manner to serve as blank.The amount of adsorbed dichlorvosand diazinonat equilibrium qe (mg/g) were calculated by principle of mass balance (equation 1)[25]: where C_o and $C_e$are initial and final equilibrium concentrations (mg/l) of the pesticide inthe aqueous phase, respectively, with V = volume of aqueous solution taken in litres and W = mass of adsorbent in grams. The Gibbs free energy values for $\Delta G^L_{ads}$and ΔG^F_{ads}kJmol^{-1} were calculated with the application of equation 2 while the Langmuir adsorption constant; K_L(mg/g), b_L (L/mg) and R_L and Freundlich adsorption constants; K_L and K_F were obtained using equations 3 and 4.

$$q_e = (C_o - C_e)x\ \frac{V}{W}1$$

III. Result And Discussion

3.1 Quantification of the pesticides, dichlorvos and diazinon

Diazinon has its maximum wavelength at 264 nm. Dichlorvos was first derivatised with ninhydrin because the molecule does not absorb light in the 200–800 nm [31] for direct spectrophotometric quantification of the compound. The dichlorvos-ninhydrin complex, (see Scheme 1), measures its intensity peak at 401 nm.



Scheme 1: A possible reaction of ninhydrin with 2,2-dichlorovinyl dimethyl phosphate(dichlorvos) to form dimethyl phosphate-ninhydrin complex

3.2 Physicochemical and morphological characterization of starch CRFs of dichlorvos and diazinon

3.2.1FTIR of starch CRFs of dichlorvos and diazinon

The FTIR spectra of blank starch, dichlorvos- and diazinon-loaded starch areshown in Figs. 2a-c; the spectral assignments are summarized in Table 1. In the blank starch spectrum (Fig. 2a), the broad band resulting from the stretching vibration of hydroxy group (O-H) appears at the 3418cm^{-1} (Shi *et al.* 2019). The sharp strong peak at 2931cm^{-1} is characteristic of the C-H stretching vibration of methylene group [13,8,32]. The two prominent absorption bands at 1639cm^{-1} and 1420cm^{-1} are due to the asymmetric and symmetric stretching vibration of carboxylate (-COO) group in the alginate moiety [8] while the peaks observed at 1156cm^{-1} and 1020cm^{-1} are assigned to C-O-C bond stretching in polysaccharides [8].The FTIR spectrum of dichlorvos-loaded starch matrix shows peaks in the region of 708 – 577 cm^{-1} for the stretching vibration band ofchloro-alkanes (C-Cl), a functional group in the active ingredient, dichlorvos[29]. It is seen that the peaks centred at 3418 and 2931 cm^{-1} in the Fig. 2a have broaden and have been shifted in the spectrum of dichlorvos-loaded starch as observed in Fig. 2b to appear at 3432 - 3388 and 2925 cm^{-1}. There is a slight broadening of the broad absorption centred at 3416 cm^{-1} and 2150 cm^{-1} and a reduction in the intensity of the bands at 1154 - 1019 cm^{-1} in diazinon-loaded starch (see Fig 2c), when compared with the blank in Fig. 2a. The peaks at 1640 cm^{-1} corresponds to the asymmetric vibration of carboxylate -COO$^-$ in alginate with overlap in the same region as the aromatic ring C-H stretching vibration in diazinon. These changes in the spectra of dichlorvos and diazinon signify interactions between the matrix and the incorporated a.i. Similar results were reported by[12,23,3].

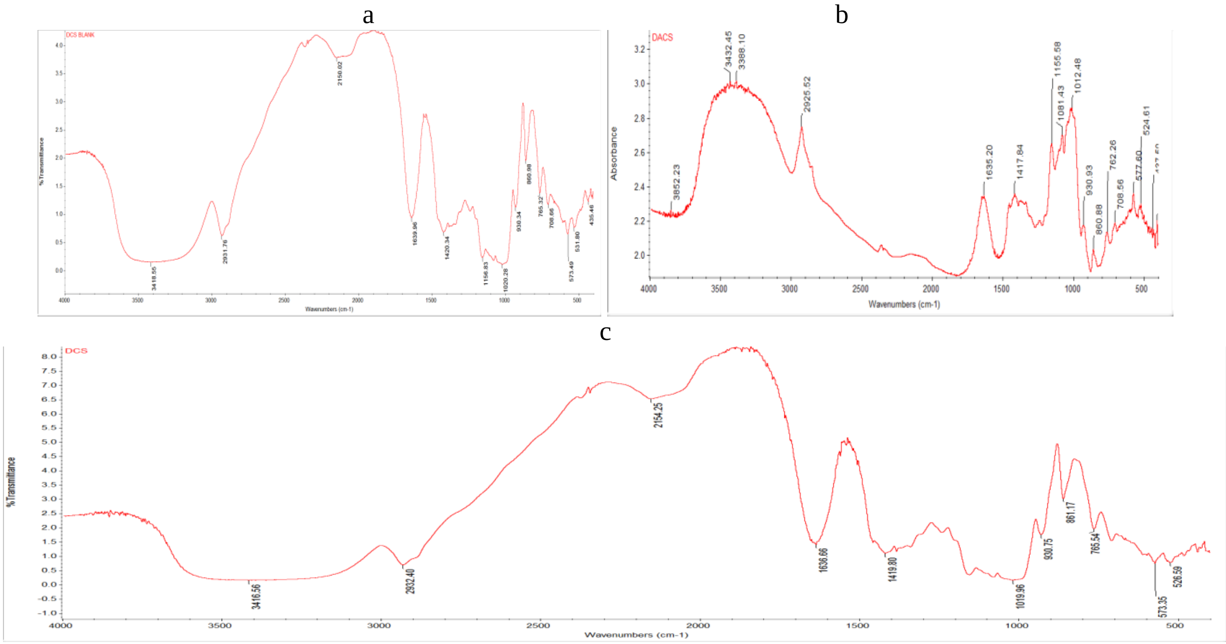


Fig. 2: FTIR spectra of: (a). blank starch, (b) dichlorvos-loaded starch and (c) diazinon-loaded starch

Spectrum	Observed wave number (cm^{-1}) in blank matrices	Observed wave number (cm^{-1}) in dichlorvos loaded- matrices	Observed wave number (cm^{-1}) in diazinon loaded- matrices	Functional group
	3418	3432-3388	3416	O-H
	2931	2925	2932, 2150	$-CH_3$
Starch	1639, 1420	1635, 1417	1646	Asymmetric and symmetric C=O (carboxylate)
	1156- 1020	1155-1012	1154- 1019	C – O – C
	-	1081	-	P=O
	-	-	930	P=S
	-	930, 860	708	P – O – R
	-	708- 577	-	C-Cl

Table 1:Major absorption bands and vibrations in FTIR spectra observed in starch, dichlorvos- and diazinon-loaded starch

3.2.2 PXRD of starch CRFs of dichlorvos and diazinon

Fig. 4a is the X-Ray pattern of blank starch cross-linked with sodium alginate used as the control. The diffractogram of the blank starch shows significant peaks at $2\theta^o$. The signals at $2\theta^o = 28^o$ and 45^o are ascribed to sodium alginate. Nnamonu*et al*.(2012) reported that the XRD of an alginate showed two peaks at $2\theta^o = 38^o$ and 44.5^o in their sorption studies of trifluralin on alginate modified starch, while Fontes*et al.* (2013) opined that the peaks at $2\theta^o = 13.7^o$, 23^o and 40^o were due to alginate in their XRD study of benzathine penicillin G-loaded alginate-starch. The broad peak at $2\theta^o = 25^o$ is ascribed to starch in the formulation which is consistent with the result of Jyothi*et al.* (2018) who observed the peaks of natural cassava starch at 23^o. The x-ray diffractogram of dichlorvos-loaded starch given in Fig. 4b reveals broader peaks at $2\theta^o = 24^o$- 28^o and 48^o - 55^o when compared with the Fig. 4a (control). Addition of dichlorvos into starch modifies the peaks of the starch matrix from sharp strong peaks to wide broad peaks, whichshows that the crystalline structure of the dichlorvos-loaded starch is more amorphous than that of the control. The PXRD spectrum of diazinon-loaded starch (Fig. 4c) showed no evidence of formation of new peaks when compared with that of the blank starch. However, the peaks at $2\theta^o$ = 24^o, 28^o and 48^o - 54^o decreased in intensity in all the diazinon-loaded starch beads. This decrease in the intensity of peaks in diazinon-loaded S100 matrix when compared with the peaks of the control is good evidence for interactions between the matrix and the active ingredient. The changes in the intensity of the bands signify interactions between the starch matrix and dichlorvos/diazinon.

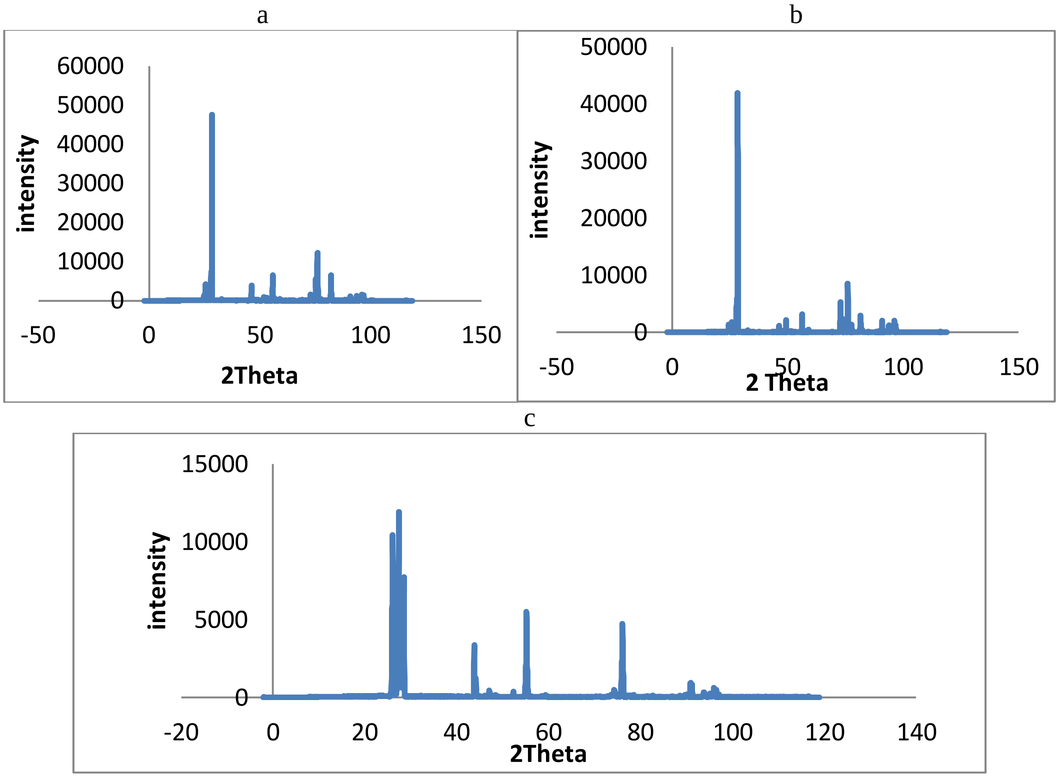
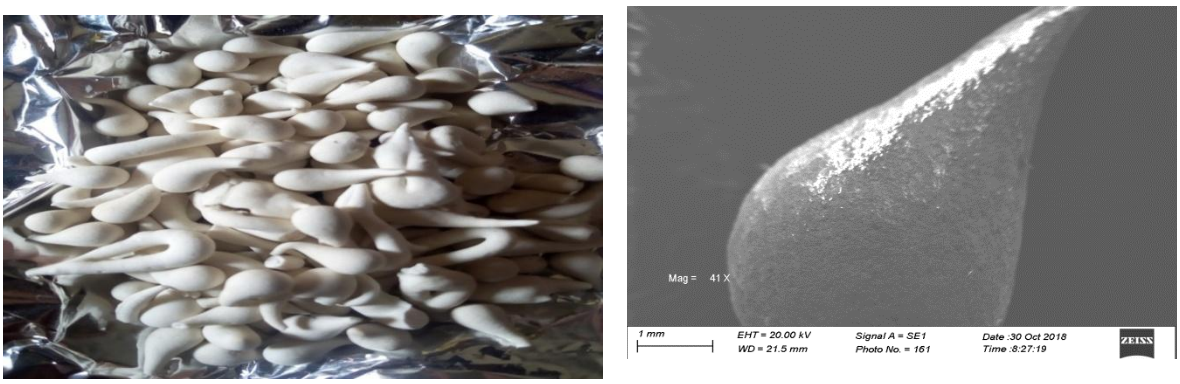


Fig. 4: PXRD spectra of: (a) blank starch (b) dichlorvos-loaded starch and (c) diazinon-loaded starch

3.3 Scanning electron microscopy

The real photograph and the SEM microgram of starch beads displayed in Figs. 3a and 3b are spherical in shape with a protruded edge, and have smooth surfaces [29]. The dichlorvos-and diazinon-loaded starch formulation given in Figs. 3c and 3d had similar cross-sectional morphology which shows moderately dense structure, big round holes and a distribution of unequal micro pores across the surface [17]. The internal structure of dichlorvos- loaded starch (see Fig. 3e) is a spatial, smooth, spherical mass of porous particles and the diazinon-loaded starch presented in Fig. 3f displays segregated, heterogeneous large lumps with cracks and crevices surface [1]. It is conceivably, that the segregated materials, crevices, cracks, spatial and micro-pores seen in the SEM micrograph of the starch CRFs in Figs. 3b - 3f are the channels for dichlorvos and diazinon molecules to diffuse easily in contact with water.

a b



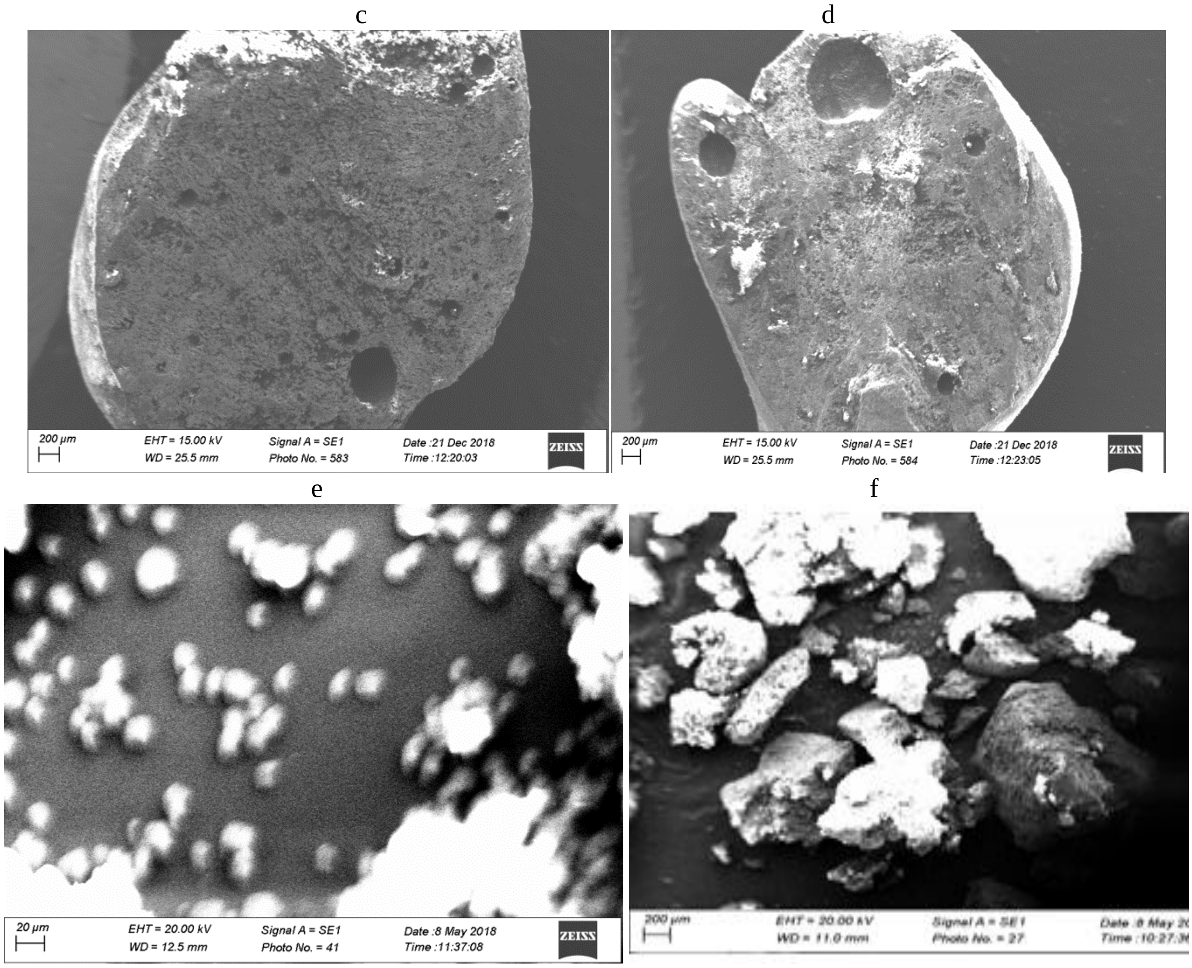


Fig. 3: (a) Photograph of starch beads and SEM micrograph showing (b) external morphology starch; (c) cross-section ofdichlorvos-loaded starch and d diazinon-loaded starch; (e) internal morphology ofdichlorvos-loaded starch and (f) diazinon-loaded starch.

3.4 ADSORPTION ISOTHERM

3.4.1 *Langmuir and Freundlich Models*

The parameters from the Langmuir and Freundlich isotherms for the adsorption of dichlorvos and diazinon on the starch surfaces are assembled in Tables 2 and 3; these parameters were extracted from the plots of $\frac{1}{q_e}$ against$\frac{1}{C_e}$, and log $q_e$versus log C_e stated in equations 3 and 4 for Langmuir and Freundlich, respectively. The correlation coefficients, R^2, for the Langmuir isotherms for dichlorvos anddiazinon adsorption are better than those for Freundlich isotherm. Furthermore, the ΔG_{ads}^{o} values obtained from the Freundlich correlation are lower than the ΔG_{ads}^{o} values usually obtained for the formation of chemical bonds as adsorptive linkage by several orders of magnitude (see table 3). TheΔG_{ads}^{F} values for chemisorption processes typically range from -80 to -400 kJ mol^{-1}[11] while the ΔG_{ads}^{F} values obtained in this study range from 2.62 - 3.99 kJ mol^{-1}and 0.20 - 0.24 kJ mol^{-1}for dichlorvos and diazinon respectively. This provides conclusive evidence that the Freundlich isotherm is not the applicable isotherm to the systemunder discussion, which supports the ideas of the Langmuir isotherm as the operational model for the adsorption of dichlorvos and diazinon on the starch surface. A similar conclusion was reached by Binh*et al*. (2019) for the adsorption of dichlorvos on coconut fibre biowastes. The K_L(mg/g) values in Table 2 shows that dichlorvos and diazinon adsorption are pH-dependent, according to the order pH 4 > pH 9 > pH 7.

Formation of strong hydrogen bonds at pH 4, [10,14] is being responsible for better adsorption of diazinon as presented in Scheme 2 and Fig. 5. This cannot be employed to explain better adsorption of dichlorvos at this pH 4 than in neutral and basic pH. The marginal difference in pHs in the Langmuir adsorption of diazinon onto starch surface may be attributed to the pK_a of diazinon = 2.4 [14] as it also influences the protonation of diazinon in pH 4 solution. As the lowest pH of this study is pH 4, the protonated diazinon may have decreased since the pK_a value of diazinon is 2.4 [15]. Under the this condition, weak hydrogen interaction may occur between the O-H moiety present in the polymeric starch matrix and the P = S, bonds in diazinon functional group as shown in Scheme 2 and Fig. 5. However, Gal *et al.* (1992) and Ku *et al.* (1998) observed that hydrogen bond on diazinon occurs at the sulphur region because the sulphur atom is more likely to hold a surrounding with higher electron density than the nitrogen atom on the diazine ring. Tiwari and Bind (2014) measure maximum adsorption at pH 4 in the removal of dichlorvos by super paramagnetic poly(styrene-co-acrylic acid) from water.

The separation factor, $R_{L,}$ obtained using equation 5, ranges from 0.056 – 0.758; on the basis of the criteria presented in Table 4, this means that the adsorption of dichlorvos and diazinon on the starch surface are favourable since $R_L < 1$. The b_L (L/mg) values, which relate to the affinity of the binding site, are typically low. The low values of b_L (L/mg) obtained show that the adsorption of both insecticide types on the starch matrix involve low energies of adsorption which is consistent with the low magnitude of ΔG^L_{ads} displayed in Table 2.

ΔG^L_{ads} (kJ mol^{-1}) values for the adsorption of dichlorvos and diazinon onto the matrix at different pH values presented in Table 3 are all negative and small in magnitude, consistent with a spontaneous adsorption process that forms a monolayer of adsorbent held together by weak physical forces. The Gibbs free energy values for $\Delta G^L_{ads}$and ΔG^F_{ads}kJmol^{-1} were calculated with the application of equation 2.The value of ΔG^o_{ads}= -4.57 kJ mol^{-1} at 298K measured by [3] for the adsorption of dichlorvos on coconut fibre is of the same magnitude as those obtained in this study.

ΔG^0_{ads} = -$RT \ln K$

2

$$\frac{1}{q_e} = \frac{1}{K_L} + \left(\frac{1}{K_L b}\right)\left(\frac{1}{C_e}\right)$$

3

$$\text{Log } q_e = \log K_F + \frac{1}{n} \log C_e$$

4

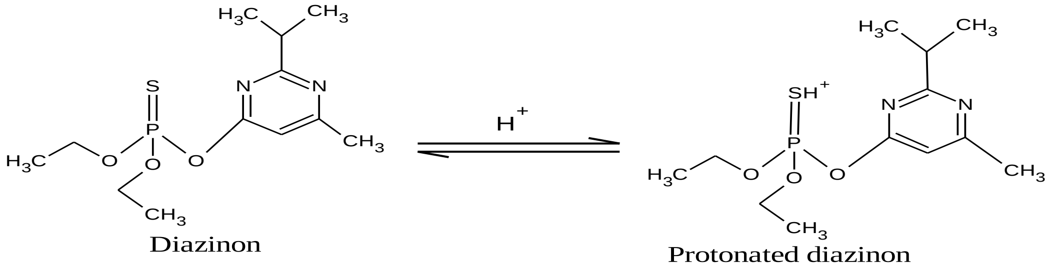
whereK_L is the Langmuir adsorption constant (mg/g); C_e = equilibruim concentration of a.i. (mg/l) in the aqueous phase; q_e= amount of a.i adsorbed per unit mass of adsorbent (mg/g); while b is the Langmuir constant which is a measure of the energy of adsorption. The K_F is the Freundlich adsorption capacity (mg/g), while n is the adsorption intensity. When n < 1, the surface of the adsorbent is heterogeneous in nature.

Table 2: Langmuir isotherm parameters for the adsorption of dichlorvos and diazinon on cow dung matrices at 298K

a.i.	Surface	K_L	b	R_L	R^2	$\Delta G^L_{ads} kJmol^{-1}$
dichlorvos	pH 4 CD100	5.405	0.025	0.758	0.982	-4.17
	pH 7	2.222	0.099	0.249	0.997	-1.97.
	pH 9 CD100	2.874	0.329	0.387	0.999	-2.61
diazinon	pH 4 CD100	2.755	0.123	0.391	0.988	-2.50
	pH 7	1.669	0.162	0.328	0.996	-1.27
	pH 9 CD100	1.672	0.179	0.306	0.993	-1.27

Table 3: Freundlich isotherm parameters for the adsorption of dichlorvos and diazinon on cow-dung matrices at 298K

	Surface	K_F	n_F	R^2	$\Delta G^F_{ads} kJmol^{-1}$
dichlorvos	pH 4 CD100	5.023	3.597	0.926	-3.99
	pH7 CD100	2.891	0.794	0.984	-2.62
	pH 9 CD100	2.977	5.605	0.854	-2.70
diazinon	pH4 CD100	1.084	2.591	0.907	-0.20
	pH 7	1.083	2.381	0.959	-0.20
	pH9 CD100	1.101	2.075	0.953	-0.24



Scheme 2: Protonation of the diazinon at pH 4

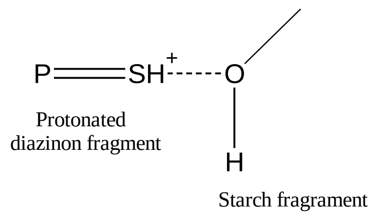


Fig. 5: Possible hydrogen bonding involving hydroxy group in starch fragments in CRFs and the protonated diazinon

$$R_L = \frac{1}{1+bC_o} \qquad 5$$

Table 4**:** the Langmuir separation factor, R_L (Ngah*et al*. 2004)

Value R_L	Meaning
$R_L = 0$	Irreversible
$0 < R_L < 1$	Favourrable
$R_L = 1$	Linear
$R_L > 1$	Unfavourable

IV. Conclusion

Controlled release beads encapsulating dichlorvos and diazinon, were formulated, using starch matrix, cross linked with alginate and $CaCl_2$. FTIR analysis of the CRFs,showedthat there is interactions between the matrix and the incorporated insecticides. The changes observed in the PXRD peaks inthe both insecticides-loaded starch beads decrease in the crystallinity nature of the starch beads. ΔG^o_{ads}valuesderived from $K_L$and K_F, have small magnitude and are all negative, describing the adsorption process as physiosorption type and spontaneous. The maximum adsorption of dichlorvos and diazinon on starch matrix were recorded at pH 4.

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