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An Evaluation of the Adsorptive Behaviour of Activated Carbon Derived from *Hyphaene Thebaica* Nut Shells for the Removal of Dichlorvos from Wastewater

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Abstract:
This work evaluates the adsorptive behaviour of activated carbon from Hyphaene thebaica nut shells treated with KOH for the treatment of water contaminated with Dichlorvos. The derived adsorbent was characterized by FTIR in order to study the surface chemistry. The batch adsorption technique was employed for the studies. Conditions for adsorption of the pesticides such as adsorbent dose, contact time, initial concentration, pH and temperature on adsorption of both pesticides onto the prepared adsorbent were optimized. The experimental data were also modeled by the Langmuir, Freundlich and Temkin adsorption isotherms. The result shows that adsorption of Dichlorvos increases with increased adsorbent dose, initial concentration, time and temperature. Optimum adsorption was observed at adsorbent dose of 50 mg, initial concentration of 250 ppm, temperature of 60 ^{0}C . and at contact time of 30 minutes. Optimum adsorption pH for Dichlorvos was found to be 2 respectively. The Langmuir isotherm model showed a better correlation (R^2 = 0.7455) compared to Freundlich and Temkin isotherm model to fit the equilibrium data. However, the experimental data values for Langmuir were inconsistent with the adsorption process as they indicated negative values. The Pseudo second order adsorption model was more suitable to describe the adsorption kinetics of the pesticide on the adsorbent. Thus, activated carbon from KOH treated Hyphaene thebaica nut shells could therefore be used effectively for the removal of Dichlorvos from waste water.

Keywords: *Adsorption, Dichlorvos, Hyphaene thebaica nut shells, Activated Carbon, Optimum, Kinetics, Equilibrium, Isotherm*

1. Introduction

Water is considered to be a vital and limited resource; population growth, industrial development and other pressures faced by developing countries have led to structured measures to ensure sustainable management of this important resource (Addagalla *et al*., 2009). Water scarcity and pollution rank equal to climate change as the most intricate environmental turmoil for the 21st century (Foo and Hameed, 2009).

Today, water pollution is one of the most important environmental problems in the world (Ghazi, 2012). The current rise in mortality is caused by the recent evolution of drug-resistant malaria, inaccessibility to effective health care facilities and the introduction of industrial by products to the environment. One of such industrial by-products threatening the environment worldwide today is pesticides residues. Reports have shown that presence of pesticide in the environment and the threat they pose to wild life and mankind have generated great concern in the past 20 years (Aminu *et al*., 2010).

The on-growing and uncontrolled use of pesticides to fight pests and improve agricultural production constitutes a risk for water quality. Thus, pesticides have been detected by monitoring surface and underground waters (Ninković *et al*., 2010).

The most frequently found types of pesticides in water bodies are derivatives of urea, pyridazinone, phenoxy acetic acid, tryazin and the group of chlorinated pesticides (Ninković *et al*., 2010).

Water treatment facilities employ a number of treatment techniques to reduce potentially harmful and disruptive contaminants, such as pesticides (Bourgeois *et al*., 2012). Several methods are available for pesticide removal such as solid-phase extraction (Souza and Lancas, 2003), photocatalysis (Franco-Garcia *et al*., 1996), photo-fenton (Fallmann *et al*., 1999), flocculation (Thebault *et al*., 1981), ion-exchange (Varhney *et al*., 1996), chlorination and ozonization (Mason *et al*., 1990) and adsorption (Tiwari and Bind, 2014).

An increasing attention has been focused on adsorption technique due to their efficiency in the removal of pollutant from aqueous solution (Chatterjee *et al*., 2010; Aksu and Kabasakal, 2006; Ru *et al*., 2007; Qiu *et al*., 2009; Cruz *et al*., 2007 and Cruz *et al*., 2008) and it is less expensive to use.

In Nigeria, *Hyphaene thebaica* nut shells are abundantly available and have no known industrial or commercial importance but rather constitutes serious environmental problem. As a result, this research investigated a readily available cheap raw material, *Hyphaene thebaica* (Doum palm) nut shells in the removal of Dichlorvos from waste water. Thus, this study is aimed at evaluating the adsorption characteristics of activated carbon prepared from *Hyphaene thebaica* nut shells for the treatment of Dichlorvos in waste water.

2. Materials and Methods

2.1. Adsorbate

2.1.1. Dichlorvos (DDVP)

Dichlorvos also known as 2,2-dichlorovinyl dimethyl phosphate (DDVP) is an organophosphate compound used to control household, public health, and stored product insects. Trade names include Apavap, Benfos, Cekusan, Cypona, Derriban, Derribante, Devikol, Didivane, Duo-Kill, Duravos, Elastrel, Fly-Bate, Fly-Die, Fly-Fighter, Herkol, Marvex, No-Pest, Prentox, Vaponite, Vapona, Verdican, Verdipor, and Verdisol. EPA has classified it as toxicity class I - highly toxic, because it may cause cancer and there is only a small margin of safety for other effects (Erdoğan, 2002). The structural formula of Dichorvos is illustrated in Figure 1.

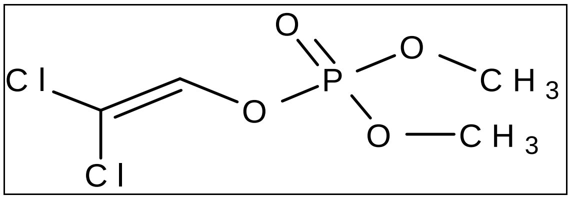


Figure 1: Structural Formula of Dichlorvos

2.2. Preparation of Activated Carbon

2.2.1. Sample Collection and Preparation

Hyphaene thebaica nut shells were collected from Kashirmo Village, Dawakil Tofa Local Government Area of Kano state, Nigeria. They were crushed and washed in order to remove the fleshy rind enclosing the hard stony kernel. The hard stony kernel was broken to get its shell used for this research. The *Hypahene thebaica* shells were chopped into pieces, washed with deionized water and sun-dried. This was oven dried at 60 ^{0}C for 24 hours. They were pulverized into powdered form.

2.2.2. Carbonization Process

100 grams of the sample was weighed into a crucible and introduced into a Muffle Furnace (Carbolite Sheffield England) which allowed a limited supply of air at 700 ^{0}C for 20 minutes. This was allowed to cool at room temperature and transferred into a 100 cm^3 beaker half filled with water. The excess water was drained and the sample was sun-dried. This process was repeated until substantial amounts of carbonized sample were obtained. The resulting sample was stored in sealed plastic containers for activation.

2.2.3. Activation Process

This was done according to the method described by Abechi *et al*. (2013) with slight modification. 20g of the carbonized sample was mixed with 25 cm^3 of KOH (1M) to form a paste. The sample was dried overnight at 120 ^{0}C . The dried sample was then pyrolysed at a predetermined temperature of 400 ^{0}C and activation time of 15 minutes in a furnace. The activated carbon was washed with 0.1 M HCl, stirred for 30 minutes to remove the base content and then washed with hot distilled water repeatedly until the washing solution nearly attained pH of 7. The prepared activated carbon was dried at 120 ^{0}C overnight, cooled and sieved into particle size of between 355µm - 425µm. This was stored in a sealed plastic container for this research.

2.3. Preparation of Stock Solution and Reagent

1cm^3 of 100 % dichlorvos was dissolved in a 100 ml volumetric flask and made to the mark with ethanol to obtain 10 ppm. Working range between 10 ppm - 50 ppm was prepared separately.

2.4. Adsorption Studies

The batch adsorption technique was employed to study the effect of adsorbent dose, contact time, initial pesticide concentration, pH and temperature. The experiment was carried out at ambient temperature (25 ^{0}C) in a water bath Shaker using 100 cm^3 conical flask as the reactor. The amount of the pesticide adsorbed was calculated as;

$$q_e = \frac{V(C_o - C_e)}{M} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

Where qe is the amount of adsorbate pesticide adsorbed in milligram per gram of the adsorbent, Co is the initial concentration of the pesticide before adsorption process, Ce is the equilibrium concentration of the pesticide in the filtrate after adsorption process and M is the mass in gram of the adsorbent, V is the volume of the solution in Litre. The percentage pesticide removal was calculated using the equation below:

$$\%\, Removal = \frac{C_o - C_e}{C_o} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots..(2)$$

2.4.1. Effect of Adsorbent Dose

The effect of adsorbent dose was studied by varying the adsorbent dose used for adsorption. The dosages of interest in milligrams are 10, 20, 30, 40 and 50. The experiment was carried out by measuring 10 cm^3 of the working solution (10 mg/L) into a 100 cm^3 conical flask and the required adsorbent dose was transferred into this conical flask. The flask was agitated for 60 minutes. This was allowed to stand for some time. The mixture was filtered immediately through a Whatman filter paper into a 120 cm^3 polyethylene bottle. The filtrate was then used for spectrophotometric test. Finally, the concentration of the residual pesticide remaining in the solution was determined using Ultra violet/visible Spectrophotometer. Thus, the optimum adsorbent dose was determined.

2.4.2. Effect of Contact Time

The effect of contact time was necessary in order to determine the time required for maximum adsorption to take place. Data generated from this study was used to describe the kinetics of the adsorption study. The effect of contact time was studied by varying the agitation time. The following agitation time in minutes that was tested is: 5, 15, 30, 45 and 60. The experiment was carried out by measuring 10 cm^3 of 10mg/l working solution into a 100cm^3 conical flask and the optimized adsorbent dose was transferred into this conical flask and agitated for the specified time. This was allowed to stand for some time. The mixture was filtered immediately through a Whatman filter paper into a 120 cm^3 polyethylene bottle. The filtrate was then used for spectrophotometric test. Finally, the concentration of the residual pesticide remaining in the solution was determined using Ultra violet/visible Spectrophotometer. Thus, the optimum contact time was determined.

2.4.3. Effect of Initial Pesticide Concentration

The effect of initial pesticide concentration was also studied by varying the initial concentration of the pesticides used for adsorption. The concentrations of interest in mg/l are 10, 20, 30, 40 and 50. The experiment was conducted by measuring 10 cm^3 of the required working solution into a 100 cm^3 conical flask and the optimized adsorbent dose was transferred into this conical flask. The flask was agitated at the optimized contact time and left to stand for some time to allow the system to equilibrate. The mixture was filtered immediately through a Whatman filter paper into a 120cm^3 polyethylene bottle. The filtrate was then used for spectrophotometric test. Finally, the concentration of the residual pesticide remaining in the solution was determined using Ultra violet/visible Spectrophotometer. Thus, the optimum concentration of the pesticides was determined.

2.4.4. Effect of pH

The effect of pH was studied by varying the pH used for adsorption at the optimized concentration. The pH of interest are 2, 4, 6 and 8. The experiment was carried out by measuring 10 cm^3 of the working solution (optimized concentration) into a 100cm^3 conical flask and the optimized adsorbent dose was transferred into this conical flask. The pH of the solution was maintained with 0.1M HCl or 0.1M NaOH and the flask was agitated at the optimized contact time. This was allowed to stand for some time to allow the system to equilibrate. The mixture was filtered immediately through a Whatman filter paper into a 120cm^3 polyethylene bottle. The filtrate was then used for spectrophotometric test. Finally, the concentration of the residual pesticide remaining in the solution was determined using Ultra violet/visible Spectrophotometer. Thus, the optimum pH of the adsorbate was determined.

2.4.5. Effect of Temperature

The effect of temperature was studied for the pesticide by varying the temperature at which the reaction takes place at optimized conditions of adsorbent dose, contact time, initial concentration and pH. The temperatures of interest are: 25 ^{0}C, 35 ^{0}C, 45 ^{0}C and 60 ^{0}C . The reactant is a 100 cm^3 conical flask agitated in a shaker water bath. This was allowed to stand for some time. The mixture was filtered immediately through a Whatman filter paper into a 120cm^3 polyethylene bottle. The filtrate was then used for spectrophotometric test. Finally, the concentration of the residual pesticide remaining in the solution was determined using Ultra violet/visible Spectrophotometer. Thus, the optimum temperature was determined.

2.5. Spectrophotometric Determination of Dichlorvos

2cm3 of the filtrate was mixed with 1cm3 of approximately 10 % sodium hydroxide and 0.5 % sodium sulphide was added after 10 minutes. This gave yellow spots which turned wine-red after some time (Daundkar *et al*., 2007). The absorbance was then measured at 435 nm using the UV/Visible spectrophotometer with deionized water as the blank.

2.6. Characterisation of Adsorbent for Surface Chemistry

To study the mechanism of Dichlorvos removal by Activated Carbon from *Hyphaene thebaica*, the active chemical groups on the adsorbent surface before and after respective pesticide adsorption were evaluated by FTIR Spectroscopy. 30mg of the finely ground activated carbon was encapsulated in 300.00mg of KBr in order to prepare the translucent sample disks used for the FTIR spectra analysis. The FTIR spectrum was recorded on a Shimadzu Fourier Transform Infrared Spectrometer (FT – IR) at the National Research Institute for Chemical Technology (NARICT) Zaria. 5 scans were collected at the spectra range of 4000 – 350 cm^{-1} with resolution of 4cm^{-1}.

3. Results and Discussions

3.1. Surface Chemistry of Adsorbent

FTIR spectral analysis was conducted for the raw, KOH activated sample and the sample after adsorption of the pesticide in order to find out the involvement of functional groups in the adsorption process. One major similarity is the band that ranged between 1500 cm^{-1}-1560 cm^{-1} for all the samples (Figures 2-4).These bands are associated with bending vibrations of N-H groups of carboxylate ions and NH_2 scissoring of primary amines. All other samples with the exception of the sample after adsorption of dichlorvos showed similarity in bands that range between 2930 cm^{-1} -2990 cm^{-1}. These bands could be attributed to the stretching vibrations of strong O-H groups of carboxylic acids and stretching vibrations of strong C-H groups of alkanes. Strong O-H stretching vibrations of alcoholic groups and weak N-H stretching vibrations of primary amines were observed at absorption band of 3417.98 cm^{-1}. The band observed at 2338.77 cm^{-1} is characteristic of P-H stretching vibrations of phosphine groups and Si-H stretching vibrations of silane. Also, a group of carbonate ions was observed at absorption band of 1487.17 cm^{-1}. Strong C=O stretching vibrations indicative of saturated aldehyde groups was observed at 1725.38 cm^{-1}. New bands in the range of 2330 cm^{-1} -2400 cm^{-1} were observed after adsorption of dichlorvos. The band detected at 2394.7 cm^{-1} is ascribed to P-H stretching vibrations of phosphine groups and Si-H stretching vibrations of silane. The occurrence of the phosphine group after adsorption is as a result of the phosphorous existing in dichlorvos as phosphate and hydrogen groups existing on the surface of the activated carbon. The new bands detected in the range of 1640 cm^{-1} - 1655 cm^{-1} after adsorption of the pesticide are characteristics of C=C stretching vibrations of alkenes, C=O stretching vibrations of cyclic amide, NH_2 scissoring of primary amines and N-H bending vibrations of cyclic amide. In addition to the strong O-H stretching modes, a weak stretching mode of N-H groups of primary amines was also detected at 3461.38 cm^{-1} after adsorption of dichlorvos.

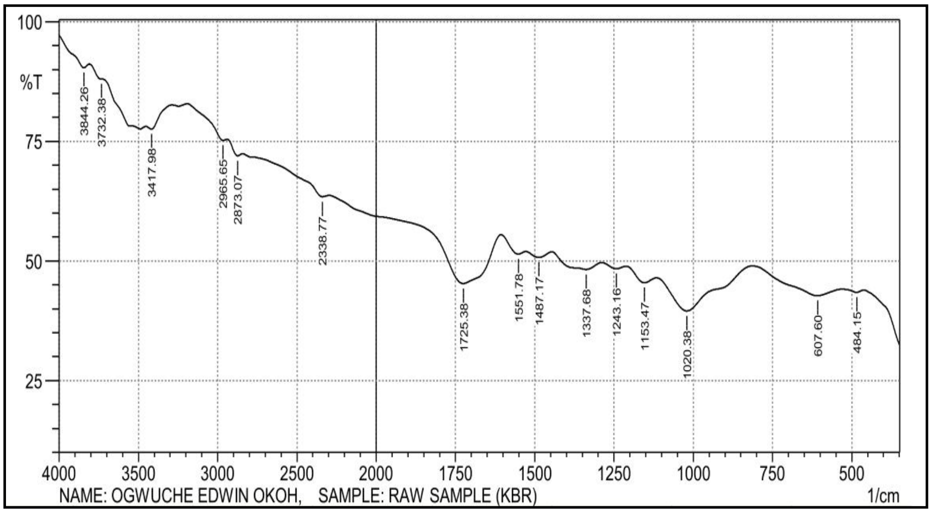


Figure 2: FTIR Spectra of Raw Hyphaene thebaica Sample

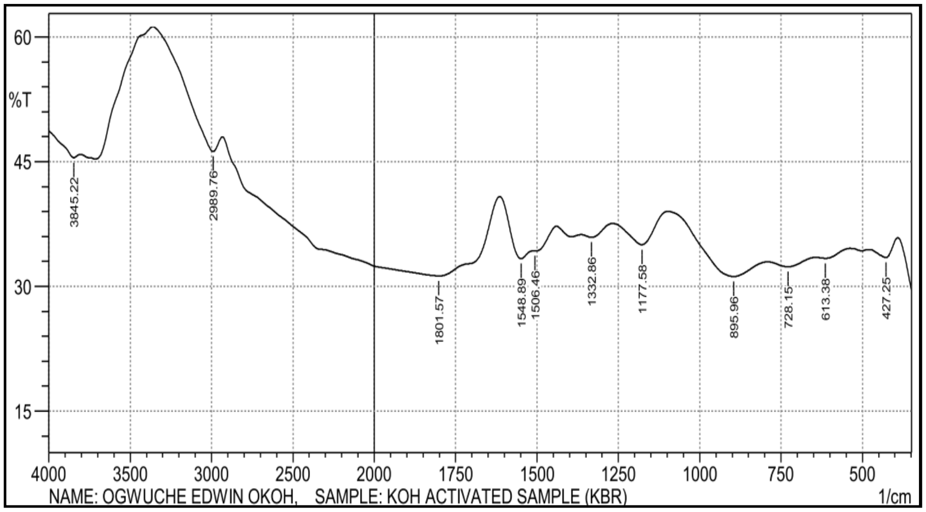


Figure 3: FTIR Spectra of KOH- Activated Hyphaene thebaica Sample

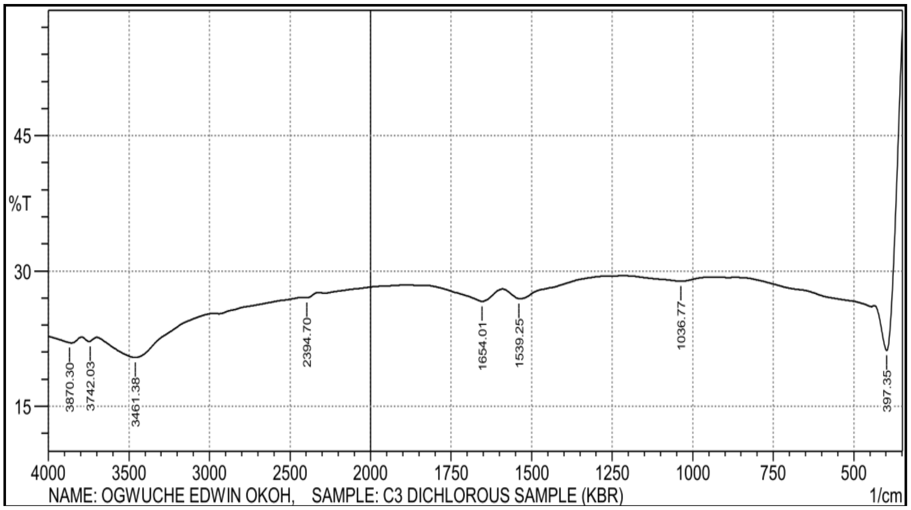


Figure 4: FTIR Spectra of KOH-Activated Hyphaene thebaica after Adsorption of Dichlorvos

3.2. Effect of Adsorbent Dosage on the Adsorption of Dichlorvos

Adsorbent dose is an important parameter in adsorption studies as it gives the optimum dosage at which maximum adsorption occurs. Figure 5 (a) shows the percentage of Dichlorvos pesticides adsorbed at varying adsorbent doses in the range of 10-50 mg at fixed pesticide concentration (50 ppm). The percentage removal increases with increasing adsorbent from 82.33% to 86.79% as dosage increased from 10 to 50 mg. It is readily understood that the number of available adsorption sites and the surface area increase by increasing the adsorbent dose and it therefore, results in the increase in amount of adsorbed pesticide (Malik *et al.*, 2007). Although percent adsorption increases with increase in adsorbent dose, it was also observed that the trend of amount adsorbed per unit mass decreased with increasing adsorbent dose. This decrease in adsorption density with increase in adsorbent dose is a result of unsaturation of adsorption sites through the adsorption process (Ozacar and Sengil, 2005; Yu *et al*., 2003). Thus, the result shows that the adsorbent dose of 50 mg which has the highest removal efficiency of 86.79% is the optimum condition for the adsorption process.

3.3. Effect of Contact Time on the Adsorption of Dichlorvos

Figure 5 (b) reveals the percentage of Dichlorvos adsorbed by the activated carbon. The rate at which Dichlorvos was adsorbed increased with an increase in contact time. The rate of adsorption of Dichlorvos is higher in the beginning with an increase in percent removal from 84.46% to 91.52% as the contact time increased from 5 to 30 minutes. However, after 30 minutes, the rate of adsorption started decreasing slowly until the contact time reached 60 minutes corresponding to 91.30% amount adsorbed. It could be explained that a large number of vacant surface sites were available for adsorption during the initial stage of the adsorption process and after the equilibrium time, the number of available vacant sites became less (Obiora-Okafor and Onukwuli, 2013). Thus, maximum removal of 91.52 % was achieved at 30 minutes depicting the optimum time for adsorption. Further increase in time after 30 minutes did not bring about any significant improvement.

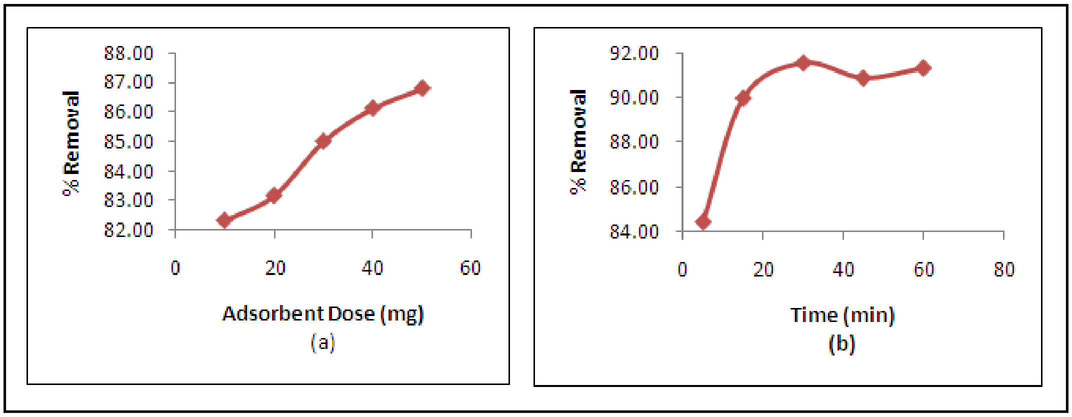


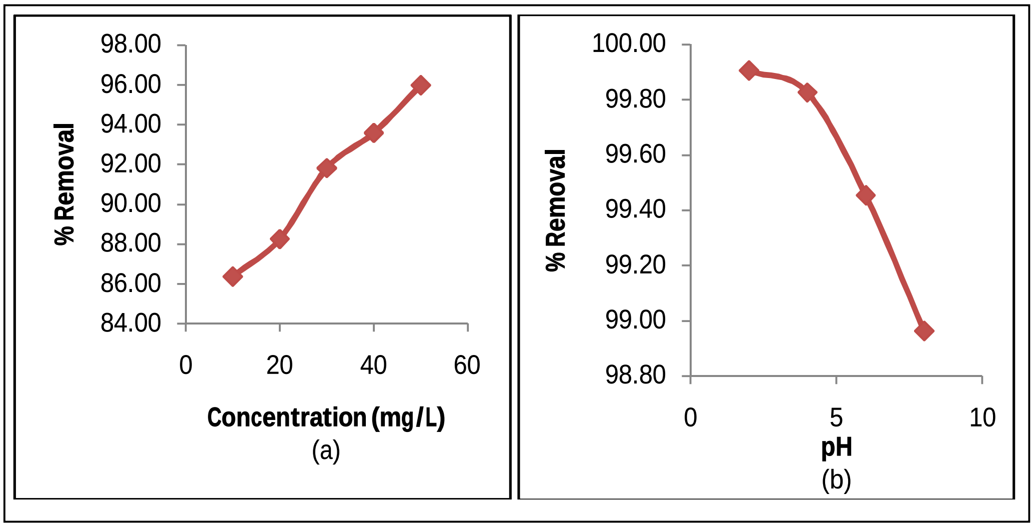
Figure 5: Effect of (a) Adsorbent Dosage and (b) Time on the Adsorption of Dichlorvos

3.4. Effect of Initial Concentration on the Adsorption of Dichlorvos

Figure 6 (a) reveals the percentage of Dichlorvos adsorbed by the activated carbon. It was observed that the amount of Dichlorvos adsorbed increases as the initial concentration increases. As the concentration of Dichlorvos increased from 50 ppm to 250 ppm, there was a corresponding rapid increase in the amount adsorbed from 86.37% to 95.97%. This percent removal was maximum at 250 ppm which is in the region of 95.97%. This increase in pesticide removal as the initial concentration of the solution is increased may be attributed the effect of increasing concentration gradient which is the main driving force for the adsorption process. That is, the increase in initial concentration of the pesticide has overcome the resistance to the mass transfer of the pesticide between the aqueous and solid phases which also enhanced the interaction between the pesticide and adsorbent (Chang *et al*., 2011). Similarly, this trend has been observed by other researchers (Tiwari and Bind, 2014) in the adsorption of dichlorvos.

3.5. Effect of pH on the Adsorption of Dichlorvos

pH is an important parameter in adsorption as it affects both the degree of ionization of the sorbate and the surface charge of the adsorbent during the adsorption process. pH influences adsorption by a way of modifying the functional groups of the adsorbent. Figure 6 (b) shows the amount of Dichlorvos adsorbed. It was observed that the amount of Dichlorvos adsorbed decreases as the pH increases. As the pH of Dichlorvos increases from 2 to 8, there was a resulting decrease in the amount adsorbed from 99.91% to 98.96%. This trend occurred possibly due to at low pH, the surface of the adsorbent would be surrounded by hydronium ions, which might enhance the dichlorvos interaction with binding sites of the adsorbent by greater attractive forces and hence improved its uptake on polar adsorbent (Memon *et al*., 2008). Lower sorption efficiency observed at basic pH range might be attributed to the increase in hydroxyl ions leading to the formation of aqua-complexes thereby retarding the adsorption (Tiwari and Kathane, 2013). At basic pH values, the dissociation degree of groups at the adsorbent surface is high and both the adsorbent and solutes occur in their negatively charged forms. Consequently, the adsorption is disfavored due to the presence of electrostatic repulsion between the molecules and the surface of adsorbent (Tiwari and Bind, 2014). Thus, optimum condition was already achieved at pH of 2 with corresponding removal of 99.91%. This observed trend is consistent with the results obtained for other adsorbent systems (Tan *et al*., 2008; Tiwari and Bind, 2014).



(a)

(b)

Figure 6: Effect of (a) Initial Concentration and (b) pH on the Adsorption of Dichlorvos

3.6. Effect of Temperature on the Adsorption of Dichlorvos

Figure 7 shows the amount of Dichlorvos removed by the adsorbent. As for Dichlorvos, it was observed that the amount of Dichlorvos adsorbed increases as the temperature increases suggesting that the adsorption was endothermic in nature. As the temperature was increases from 25 °C to 60 °C, there was also corresponding progressive increase in the percent removal from 99.94% to 99.99%. This behavior could be attributed to better interaction between the pesticide and adsorbent, creation of new adsorption sites and increased intra-particle diffusion at higher temperatures. Thus, optimum condition was achieved at temperature of 60 °C corresponding to 99.99% removal.

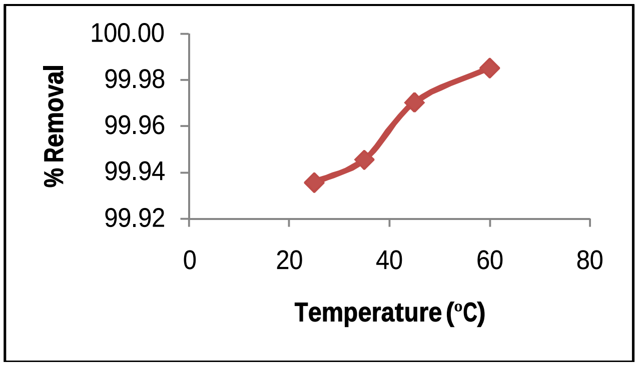


Figure 7: Effect of Temperature on the Adsorption of Dichlorvos

3.7. Equilibrium Adsorption Studies

3.7.1. Adsorption Isotherms

Adsorption Isotherms describe how solutes interact with adsorbents. The applicability of isotherm models to the adsorption study done was compared by judging correlation coefficients, R^2 values. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes (Tan *et al.*, 2008). The equilibrium data obtained on effect of initial pesticide concentration were applied on linearized Langmuir, Freundlich, and Temkin isotherm equations.

3.7.2. Langmuir Adsorption Isotherm

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes that adsorption occurs uniformly on the active sites of the adsorbent, and once an adsorbate occupies a site, no further adsorption can take place at that site. Based upon these assumption, Langmuir represented the following equation:

$$q_e = \frac{q_{max} b C_e}{1 + bC_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (3)$$

The Langmuir adsorption parameters were determined by transforming the Langmuir equation (5.2) into linear form:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where; q_e is the amount of adsorbate adsorbed per gram of dried adsorbent at equilibrium (mg adsorbate/g of dried adsorbent), q_{max} is the maximum monolayer coverage capacity (mg/g), b is Langmuir constant or adsorption coefficient or the adsorption affinity (L/mg) for binding of adsorbate on the adsorbent sites and C_e is equilibrium (residual) adsorbate concentration in solution after adsorption (mg/L). The values of q_{max} and b can be calculated from the intercept $\left(\frac{1}{q_{max}}\right)$ and slope $\left(\frac{1}{q_{max}b}\right)$ of the plot $\frac{1}{q_e}$ against $\frac{1}{C_e}$ as illustrated in Figures 4.14 (Gupta and Rastogi, 2007).

The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter, R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter. This is given as:

$$R_L = \frac{1}{1 + bC_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (5)$$

Where C_o is the initial concentration and '*b*' is the constant related to the energy of adsorption (Langmuir constant). The values of R_L indicate the nature of the isotherm. It has been reported that $R_L>1$ indicate unfavourable adsorption, $R_L=1$implies a linear shape isotherm, $0<R_L<1$ and $R_L=0$ indicates favourable and irreversible adsorption isotherm respectively (Shabudeen *et al*., 2006). The Langmuir isotherm constants, coefficient of determination, R^2, and separation factor, R_L, are listed in Table 1 for Dichlorvos adsorption.

From this work, the correlation coefficient (R^2=0.7455) obtained for Dichlorvos adsorption fit to the Langmuir isotherm. However, as a result of the negative values for the Langmuir isotherm constants, this imply that this model is not suitable to explain the adsorption process, since these constants are indicative of the surface binding energy and monolayer coverage (Ramakrishna and Viraraghavan, 1996; Maarof *et al*., 2003; Alves Fungaro *et al*., 2009; Kiurski *et al*., 2011). This suggests that some heterogeneity in the surface or pores of the activated carbon synthesized from *Hyphaene thebaica* nut shell will play a role in pesticide adsorption. The separation factor, R_L, also indicates a negative value suggesting that the adsorption of the pesticides on activated carbon synthesized from *Hyphaene thebaica* was difficult (Bhavna *et al*., 2011).

3.7.3 Freundlich Adsorption Isotherm

The Freundlich isotherm model is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. That is, it is commonly used to describe the adsorption characteristics for the heterogeneous surface (Hutson and Yang, 2000). It is the relationship between the amounts of pesticide adsorbed per unit mass of adsorbent, q_e, and the concentration of the pesticide at equilibrium, C_e . This is given by the empirical equation proposed Freundlich:

$$q_e = K_f \, C_e^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots... (6)$$

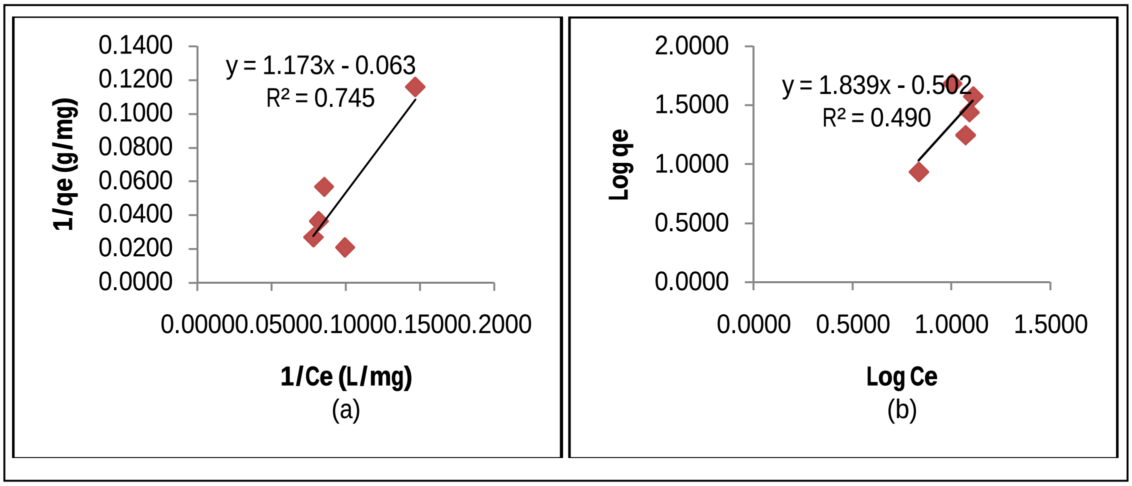
Its linearized form is given as:

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where, q_e is the amount of adsorbate adsorbed per unit weight of biosorbent, K_f is Freundlich Constant measuring adsorption capacity(L/mg), C_e is equilibrium concentration of the adsorbent in solution(mg/l), n is constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent.

Figure 8 (b) shows Freundlich isotherm model of the pesticides adsorption. The isotherm constants and correlation coefficients, R^2, are listed in Table 1. A plot of lnq_e against lnC_e gives a straight line with a slope, $1/_n$ and an intercept, lnK_f. The K_f value increases with the total adsorption capacity of the adsorbent to bind the adsorbate. The numerical value of n is a useful index to determine favorability of the adsorption. Specifically, the linear least-squares method and the linearly transformed equations have been widely applied to correlate sorption data where $1/_n$ is a heterogeneity parameter, the smaller $1/_n$, the greater the expected heterogeneity. This expression reduces to a linear adsorption isotherm when $1/_n$ = 1. If n lies between 1 and 10, this indicates a favorable adsorption process (Goldberg, 2005).

The experimental data showed freundlich constants, K_f and n to be 0.31 and 0.54 respectively. This was evidenced by a poor correlation coefficient, R^2, of 0.4907. Thus, the adsorption isotherm for dichlorvos adsorption cannot be fitted using the freundlich model due its poor correlation coefficient.



(a)

(b)

Figure 8: (a): Langmuir and (b) Freundlich Isotherm for the Adsorption of Dichlorvos

3.7.4. Temkin Adsorption Isotherm

This isotherm contains a factor that explicitly takes into account of the adsorbent–adsorbate interactions. It based on the assumption that due to the adsorbate-adsorbate repulsions the heat of adsorption of all the molecules in the layer decreases linearly with the coverage of molecules and the adsorption of adsorbate is uniformly distributed. (Temkin and Pyzhev, 1940). The model is given by the following equation (Temkin and Pyzhev, 1940):

$$q_e = BlnA_t + BlnC_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

B is further determined from the expression as:

$$B = \frac{RT}{b_T} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. (9)$$

Where A_T is the Temkin isotherm equilibrium binding constant (L/g), b_T is the Temkin isotherm constant, R is the universal gas constant (8.314J/mol/K), T is the Temperature at 298K and B is the constant related to heat of adsorption(J/mol).

Figure 9 shows the plot of the Temkin isotherm model for the adsorption of Dichlorvos from aqueous solution onto the *Hyphaene thebaica* shell based activated carbon. The Temkin isotherm data are also shown in Table 1. The values of correlation coefficient, R^2, B and A_T for Dichlorvos adsorption were estimated to be 0.2607, 30.84 and 1.45 respectively. The poor correlation coefficient, R^2, for Dichorvos indicates that the model does not fit into the data.

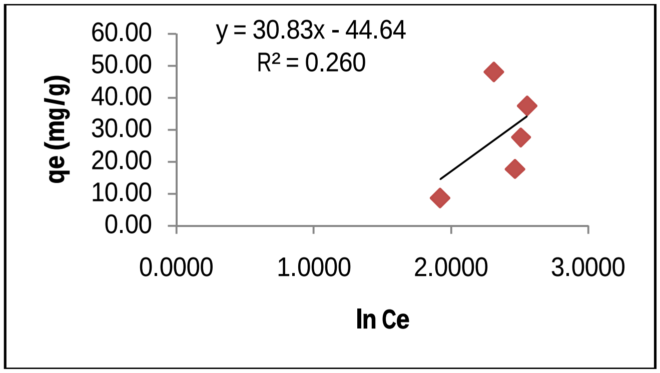


Figure 9: Temkin Isotherm for the Adsorption of Dichlorvos

Isotherms	**Parameters**	**Values**
	q_{max}	-15.67
Langmuir	b	-0.0541
	R^2	0.7455
	K_f	0.31
Freundlich	n	0.54
	R^2	0.4907
	B	30.84
Temkin	A_T	1.45
	b_T	80.34
	R^2	0.2607

Table 1: Correlation Parameters of Langmuir, Freundlich and Temkin Isotherms

Where R^2 is the correlation coefficient, q_{max} is the maximum pesticide uptake (mg/g), b is the Langmuir constant (l/mg), R_l is the separation factor, K_f is the Freundlich Constant measuring adsorption capacity (L/mg), and n, is a constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent), A_T is the Temkin isotherm equilibrium binding constant (L/g), is the Temkin isotherm constant and B is the constant related to heat of adsorption(J/mol).

3.8. Kinetic Adsorption Studies

In order to investigate the mechanism of adsorption and potential rate controlling step, such as mass transport and chemical reaction processes, pseudo-first-order and pseudo-second-order kinetic models were used to test the equilibrium data obtained from effect of contact time in order to investigate the mechanism of the pesticide adsorption . Moreover, information on the kinetics of pesticide uptake is required for selecting optimum conditions for full scale batch pesticide removal processes. A kinetic study with different time intervals, fixed pesticide and adsorbent concentration was performed and the results obtained are presented in Table 2. The pseudo-first-order equation is generally expressed as follows (Omri *et al.*, 2012).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Where q_e and q_t are the amount of adsorbate adsorbed on adsorbent at equilibrium and time *t*, respectively (mg/g), and k_1 is the rate constant of first order adsorption (min^{-1}).

The plot of $\log(q_e - q_t)$ versus t will give a straight line and the value of k_1 can be evaluated from the slope of the graph, $-\frac{k_1}{2.303}$, while $q_{e\text{(calculated)}}$ is obtained from the intercept, log q_e, of the graph as illustrated in Figure 10 (a).

The linearized second-order kinetic model is expressed as (Franca *et al.*, 2009):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Where, k_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1}min^{-1}). The plot of $\frac{t}{q_t}$ versus t will give a linear relationship with $\frac{1}{q_e}$ and $\frac{1}{k_2 q_e^2}$ as a slope and intercept, respectively. The values of q_e and k_2 can be determined from the slope and intercept as illustrated in Figures 10 (b).

Table 2 shows comparison between adsorption rate constants, q_e estimated and correlation coefficient associated to the pseudo – first and – second order adsorption of the pesticides. Figure 10 represents pseudo-first and second-order kinetics modeling of Dichlorvos adsorption on *Hyphanene thebaica* nut shell based activated carbon respectively.

The experimental adsorption capacity of Dichlorvos is 9.15 mg/g respectively. The corresponding calculated adsorption capacity using the pseudo-first-order model is 0.98 mg/g respectively while the calculated adsorption capacities using the pseudo-second-order model is 9.18 mg/g. The calculated adsorption capacity of the pesticide by the pseudo-second-order model show close agreement with their respective experimentally determined adsorption capacity unlike pseudo-first-order, where there is large difference between the experimental and calculated adsorption capacities of both pesticides. The correlation coefficients, R^2 values for the pseudo-second-order adsorption model of the pesticide is higher ($R^2 =$1.000) than that of pseudo first order adsorption model ($R^2 <$0.600). However, the correlation coefficient values, R^2, and calculated adsorption capacity of the pesticide by pseudo-first-order model is not satisfactory, which suggest that it is dependent on initial concentration. Hence, Pseudo second order adsorption model is more suitable to describe the adsorption kinetics of Dichlorvos on the adsorbent and this relies on the assumption that adsorption may be the rate-limiting step (Gupta and Rastogi, 2007). Therefore, the rate limiting step is an indication of chemisorption.

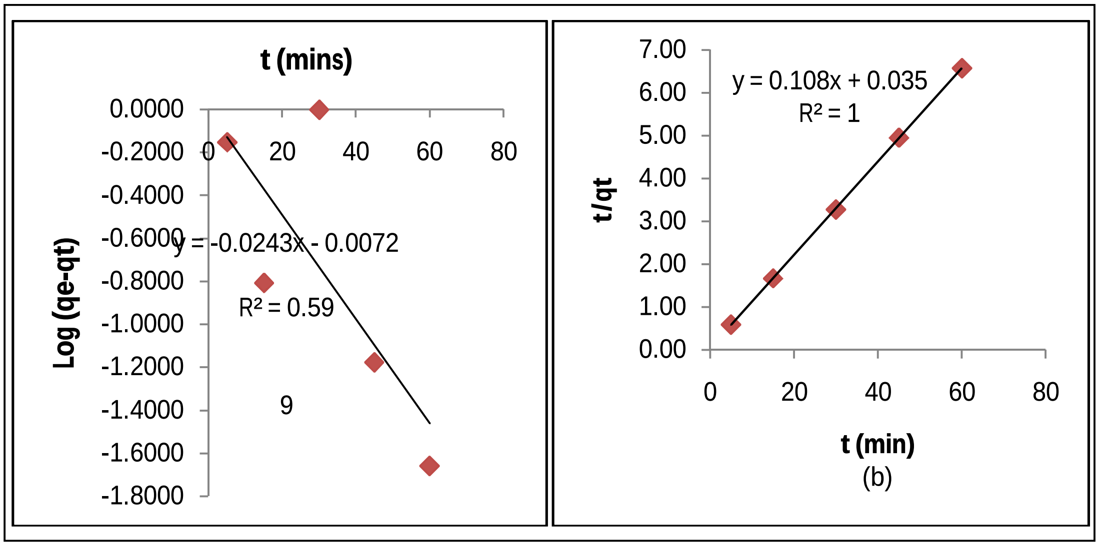


Figure 10: (a) Pseudo First-Order Model and (b) Pseudo Second-Order Model for Dichlorvos Adsorption

	Pseudo-First-Order Model					**Pseudo-Second-Order Model**		
	R^2	$q_{e\ (cal)}$	k_1		$q_{e\ (exp)}$	R^2	$q_{e\ (cal)}$	k_2
Dichlorvos	0.599	0.98	0.0560		9.15	1.000	9.18	0.3305

Table 2: Correlation Parameters of Kinetic Model for Dichlorvos Adsorption

4. Conclusion

An attempt was made to examine the adsorption characteristics of activated carbon prepared from *Hyphaene thebaica* nut shells for the removal of Dichlorvos from waste water. In doing so, the conditions for adsorption of the pesticides were optimized and evaluation of the performance of the adsorbent using selected isotherm models such as Langmuir, Freundlich and Temkin was made. The mechanism of adsorption of the pesticides from kinetic data was also made.

The study indicated the suitability of activated carbon derived from *Hyphaene thebaica* nut shells for the removal of Dichlorvos from waste water. The selected adsorbent may be viewed as a useful material while considering the economic aspect of waste water treatment.

The adsorbent exhibited good surface chemistry suitable for enhancing the activity in the adsorption process. As such, hydroxyl, carbonyl and amine groups are majorly responsible for the pesticide adsorption.

The adsorption of Dichlorvos by *Hyphaene thebaica* derived activated carbon is dependent on the initial dichlorvos concentration with an optimum concentration of 250 ppm. Thus, Pseudo second order adsorption model is more suitable to describe the adsorption kinetics of the pesticide on the adsorbent.

The adsorption of Dichlorvos was found to have a pH of 2 and adsorbent dose of 50 mg at saturation point. Batch experiments reveal that the dilute solutions of Dichlorvos solutions reached equilibrium after 30 minutes and at optimum temperature of $60\ ^\circ\mathrm{C}$. The equilibrium isotherm studies demonstrates the model which fits better is the Langmuir isotherm ($R^2 = 0.7455$) even though negative experimental data were observed which makes it unsuitable to describe the adsorption process.

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