



Research Paper

Effect Ofavocado Pear (*Persea Americana*) Peelsbiochar As Adsorbent In The Removal OfdichlorovinylDimethlyphosphate Pesticide In Contaminatedsoil

¹Awolo S. N.,²Osu, C. I.,³Ideriah T.J.K. and ⁴Okafor, C.

^{1, 4}Chemistry Department, Rivers State University, Port Harcourt.

²Chemistry Department, University of Port Harcourt.

³Institute of Pollution Studies, Rivers State University, Port Harcourt.

ABSTRACT

This research was conducted to evaluate the effectiveness of avocado pear biochar (APB) on the removal of DichlorovinylDimethlyPhosphate (also known as DDVP or Dichlorvos) pesticide in soil through bioremediation processes. Biochar prepared from avocardo pear was pyrolysed at 500°C. Experimental procedures were conducted to evaluate the effectiveness of adding biochar to soil by determining the concentration of Dichlorvos with effect of Contact time, Dosage and temperature using GC-MS. Effects of Contact time, Dosage and temperature on adsorption efficiency of APB were investigated. The results showed percentage removal of DDVP increased at different interval of time (34.52%, 51.10, 53.05% and 54.25% between 30minutes, 60minutes, 90minutes and 120 minutes respectively), dosage (62.43%, 83.15%, 90.91% and 95.65% at 2.0gram, 2.5gram, 3.0gram and 5.0gram respectively) and temperature (2.20%, 45.54%, 60.96% and 62.11% at 40°C, 60°C, 80°C and 100°C respectively). The Langmuir and Freundlinch isotherm models described adsorption of DDVP and had best fit of $R^2 = 0.9337$ and 0.9155 respectively.

Keywords: Remediation, Soil, Avocardo Pear, Biochar, ContactTime, Dosage, Temperature

Received 09 Sep., 2024; Revised 23 Sep., 2024; Accepted 25 Sep., 2024 © The author(s) 2024.

Published with open access at www.questjournas.org

I. INTRODUCTION

The escalating need and utilization of energy globally, alongside with fossil fuel depletions has made the exploration and utilization of renewable energy sources to be of main concern. Just as pyrolysis is being recognised as one of the most assuring thermo-chemical conversion of biomass to bioenergy products, biomass is considered a possible renewable energy source (Özçimen & Karaosmanoğlu, 2004). The pyrolysis of biomass waste (burning in the absence of oxygen) gives rise to three products: a solid, liquid (bio-oil) and gas (Bridgwater, 2003). According to Azargohar & Dalai, (2006) biochar may be referred to as a solid product of pyrolysis; Sohi *et al.* (2010) defined it as biomass-derived char meant particularly for soil application. We suggest that the word biochar be termed a solid residual from thermo-chemical transformation of biomass whose intending purpose is to necessitate carbon sequestration which refers to biochars' ability to prevent carbon from entering the atmospheric CO₂ pool by keeping it in a more stable C pool (Goldberg, 1985; Kuhlbusch & Crutzen, 1995; Lehmann *et al.*, 2006).

Biochar applications for soil amendment started over 2500 years ago, when biochar was used by local Indians to fertilize small plots of land in highly infertile soils in the Amazon. This practice was known as “Terra Preta” (Wayne, 2012). Report reveals that Terra Preta soils still remain extraordinarily fertile after being compared with neighbouring soils, even after so many centuries. This exceptionally finding has brought so much attention to biochar’s capability of long-term microbial activity as well as carbon sequestration (Komang & Orr, 2016).

Biochar-soil amendments particularly in farmland is supported both as an important means of improving soil fertility and also sequestering carbon. In several instances, research has showed that biochar has high affinity for organic pollutants. Yang & Sheng, (2003) stated that the amount of diuron adsorbed by wheat char/ash was 500–3000 times more than that of a loamy-silt soil (2.2% organic carbon). Several studies have revealed biochar to be an effective sorbent for numerous herbicides including, ametryn, atrazine, acetochlor, diuron, simazine and benzonitrile. Biochar's highly sorptive nature may either be beneficial or problematic depending on how the material is utilized.

Several soils obtaining new applications of biochar has been evaluated, yet it is not clear on how, and if rapidly, the capability of biochar in pesticides sorption will change with time. Biochar in soils might experience high biogeochemical interactions due to their highly reactive nature and with time, access to biochar sorption sites might be blocked (Zhou & Song, 2004).

In agricultural production systems, soil serves as a fundamental resource. Soil quality has been threatened for several decades through substantial usage of pesticides, thereby imposing toxic effects on living organisms (Zhou *et al.*, 2004; Vangronsveld *et al.*, 2009). However, remediation of soils through suitable environmental alternatives in restraining the existence of contaminated soil seems to be a suitable way to address soil contamination (Mench, *et al.* 2010; Powlson *et al.* 2011).

Biochar could be used to recover contaminated areas and brownfields as it increases soil fertility and improves growth of crops, trees and other flora. Also, it enhances the ground's capability of handling drought and flooding. Biochar can likewise reduce the amount of heavy metals as well as other pollutants in soils and prevents them from getting into water bodies. (Schmidt *et al.*, 2014; Hagner, 2016).

This study is centred on biochar production from avocado pear peels and its use as an adsorbent for the remediation of Dichlorovinyl Dimethyl phosphate (DDVP) contaminated soil.

II. MATERIALS AND METHODS

Biochar Production

Avocado Pear Peels (APP) were obtained from the market in Port Harcourt. The avocado pear biochar (Figure 1) was prepared using a locally made pyrolysis unit (oven) at temperature of 500°C with optimum pyrolysis time of one hour (Martinsen *et al.*, 2015).



Figure 1: Avocado pear biochar (APB)

Soil

Loamy soil (Figure 2), containing approximately 16% clay, 40% sand and 43% silt, pH 6.0 and organic carbon 2.52 % was used for this study and was sampled between 0-20 cm depth from a farming area at the University of Port Harcourt, Rivers State, Nigeria using soil auger and transported to the laboratory. The soil was first air-dried after which it was further dried using a heat-fan (1 day in room temperature and 2 x 1 hour with heat fan), sieved with 2.0 mm mesh sieve and stored at room temperature prior to usage.



Figure 2: soil in experiment

Method of Analysis

In obtaining the biochar residue, 20 ml of DDVP was measured into a conical flask and mixed with 10 ml distilled water and 10 g soil. 10 g of unamended biochar was added to the mixture and was further filtered and dried.

Determination of Dichlorvos Concentration using GC-MS

The effect of adding biochar to the contaminated soil was evaluated by determining the concentrations of Dichlorvos (the contaminant).

The experimental procedures were in three stages: (i) effect of contact time on addition of biochar (ii) effect of dosage (iii) effect of temperature on addition of biochar.

The initial concentration of Dichlorvos (control) was prepared by measuring 10 g of soil and 20 ml of Dichlorvos into a conical flask and mixed with 10 ml of distilled water. The soil was added to the mixture and thoroughly mixed. The mixture was filtered with a micro filter paper and placed in 10 ml plastic bottle and labelled C₀.

Effect of Contact Time

Dichlorvos, 20ml was measured into four different conical flasks and mixed with 10 ml of distilled water each. 10 g of soil and 1g of biochar were added to each mixture. The mixtures were corked and arranged in a shaker at time interval of 30 min, 60 min, 90 min, and 120 min respectively. The mixtures were filtered with a filter funnel together with a micro filter paper at their respective time. All filtrates were retained in 10 ml plastic bottles labelled t₁, t₂, t₃, and t₄. The concentrations of compounds were determined using Gas chromatography - Mass Spectrometer (SHIMADZY GC-MS – Q P 2010 PLUS).

Effect of Dosage

Dichlorvos, 20 ml was measured into four different conical flasks mixed with 10 ml distilled water respectively and 10 g of soil was added to each mixture. To the first mixture was added 2.0 g of APB, the second 2.5 g, the third 3.0 g and the fourth 5.0 g of APB respectively. The mixtures were corked and placed in a shaker for 90 min. They were all filtered using a filter funnel together with a micro filter paper. All filtrates were placed in 10 ml plastic bottles labelled D₁, D₂, D₃, and D₄. The concentrations of compounds were determined using Gas chromatography - Mass Spectrometer (SHIMADZY GC-MS – Q P 2010 PLUS).

Effect of Temperature

Dichlorvos, 20ml was measured into four different conical flasks and mixed with 10 ml distilled water respectively and 10 g of soil was added to each mixture. 1g of APB was added to the mixtures and placed in four different water baths at different temperatures of 40°C, 60°C, 80°C and 100°C respectively for 90 minutes. The temperatures were continuously checked using a thermometer to ensure it does not exceed the required temperature. At elapsed time, all filtrates were placed in 10 ml plastic bottles labelled T₁, T₂, T₃ and T₄. The concentrations of compounds were determined using Gas chromatography - Mass Spectrometer (SHIMADZY GC-MS – Q P 2010 PLUS).

III. RESULTS AND DISCUSSION

Table 1. Effect of Contact Time on the Removal of Dichlorvos from Soil Using APB

Sample	Time (min)	Co (mg/l)	Ce (mg/l)	% Removal (Co – Ce) / Co *100
t ₁	30	284800	186500	34.52%
t ₂	60	284800	139200	51.10%
t ₃	90	284800	133700	53.05%
t ₄	120	284800	130300	54.25%

Table 2. Effect of Dosage on the Removal of Dichlorvos from Soil Using APB

Sample	Dosage (g)	Co (mg/l)	Ce (mg/l)	% Removal (Co – Ce) / Co *100
D ₁	2.0	284800	107000	62.43%
D ₂	2.5	284800	48000	83.15%
D ₃	3.0	284800	25900	90.91%
D ₄	5.0	284800	12400	95.65%

Table 3. Effect of Temperature on the Removal of Dichlorvos from Soil Using APB

Sample	Temp (°C)	Co (mg/l)	Ce (mg/l)	% Removal (Co – Ce) / Co *100
T _{P1}	40	284800	278600	2.20%
T _{P2}	60	284800	155100	45.54%
T _{P3}	80	284800	111200	60.96%
T _{P4}	100	284800	107900	62.11%

Table 4. Freundlich and Langmuir isothermal parameters for the adsorption of DDVP from soil using APB

Co (mg/L)	Ce (mg/L)	Co - Ce (mg/L)	V/M (L/mg)	q _e	Inq _e	InCe (mg/L)	Ce/q _e
284800	278600	6200	0.02	124	4.820282	12.53753	2246.774
284800	155100	129700	0.02	2594	7.860956	11.95183	59.79183
284800	111200	173600	0.02	3472	8.152486	11.61909	32.02765
284800	107900	176900	0.02	3538	8.171317	11.58896	30.49746

Table 5. Freundlich and Langmuir correlation coefficients for the adsorption of DDVP from soil using APB

Freundlich	Langmuir
$R^2 = 0.9155$	$R^2 = 0.9337$
$1/n = 0.3$	$R_L = 0.003$

Table 6. Adsorption kinetics parameters for the adsorption of DDVP using APB

Time (min)	t1/2	Co (mg/l)	Ce (mg/l)	Co-Ce (mg/L)	V/M(l/m g)	qt	Qe	t/qt	qe-qt	ln(qe-qt)	R ²
30	5.47722 6	284800	186500	98300	0.02	196 6	0.30 8	0.01525 9	- 1965.6 9	Nil Nil	K ₁ =
60	7.74596 7	284800	139200	145600	0.02	291 2	0.30 8	0.02060 4	- 2911.6 9	Nil 0.987	K ₂ =
90	9.48683 3	284800	133700	151100	0.02	302 2	0.30 8	0.02978 2	- 3021.6 9	Nil 0.810	K ₃ =
120	10.9544 5	284800	130800	154000	0.02	308 0	0.30 8	0.03896 1	- 3079.6 9	Nil	

Table 7. Thermodynamic parameters for the adsorption of DDVP using APB

Temp. (K)	1/Temp.	K ^o	ln K ^o	ΔG^o (KJmol ⁻¹)	ΔH^o (KJmol ⁻¹)	ΔS^o (Jmol ⁻¹)
313	0.0032	0.00045	-7.70626	2196.18		
333	0.0030	0.01673	-4.79055	1452.45	7877.92	18.6316
353	0.0028	0.03122	-3.46670	1114.23		
373	0.0027	0.03279	-3.41763	1160.69		

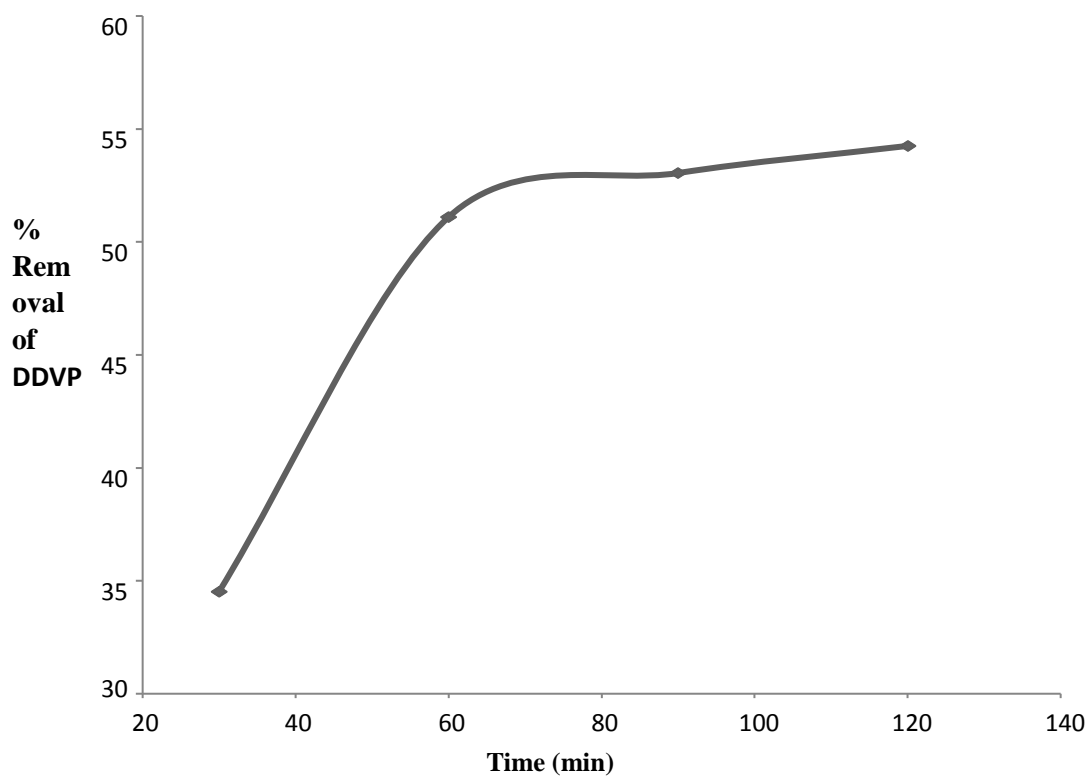


Fig. 3 Effect of time on the removal of DDVP from soil using APB

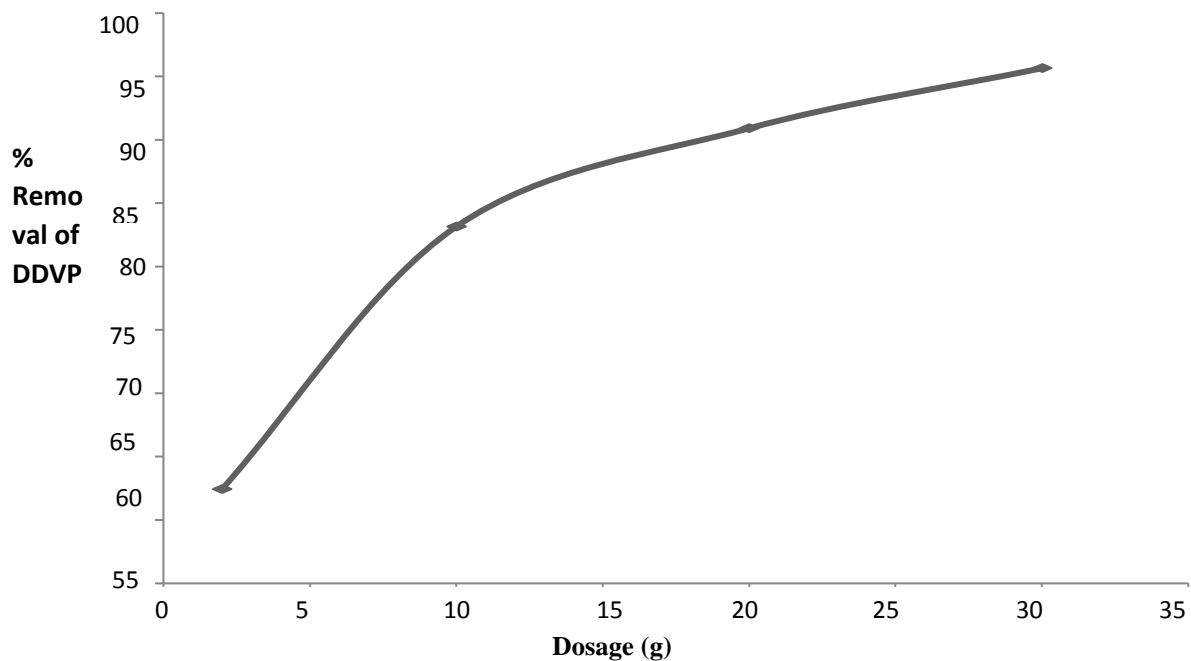


Fig 4 Effect of dosage on the removal of DDVP from soil using APB

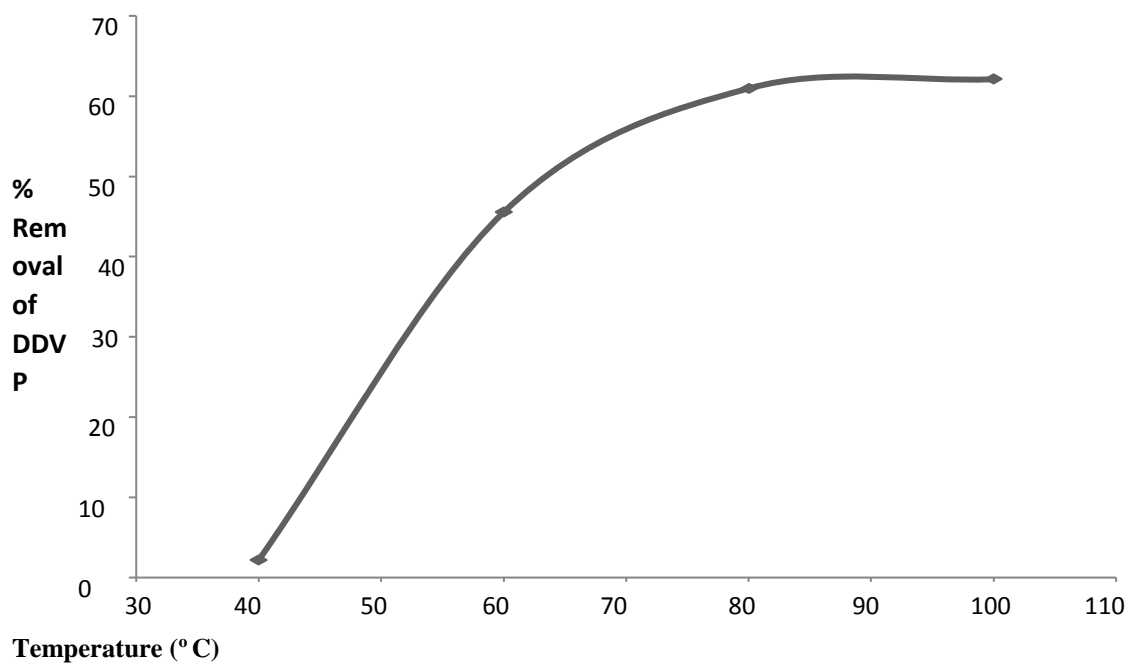


Fig. 5. Effect of temperature on the removal of DDVP from soil using APB

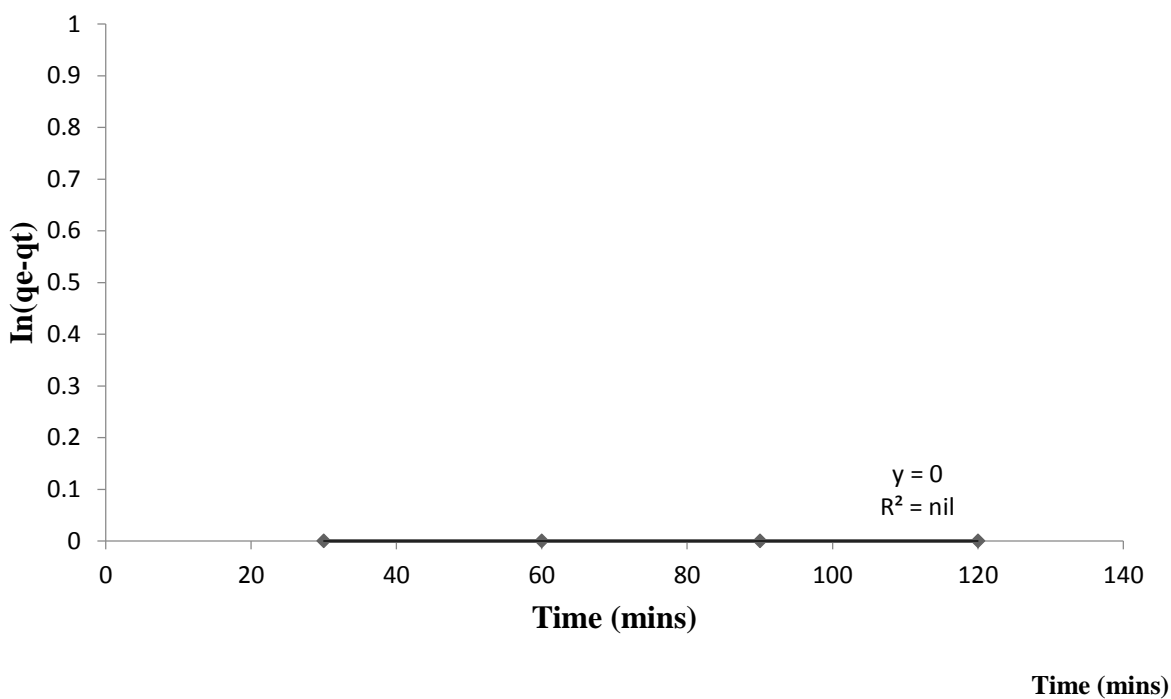


Fig. 6. Pseudo first order kinetics for the removal of DDVP from soil using APB

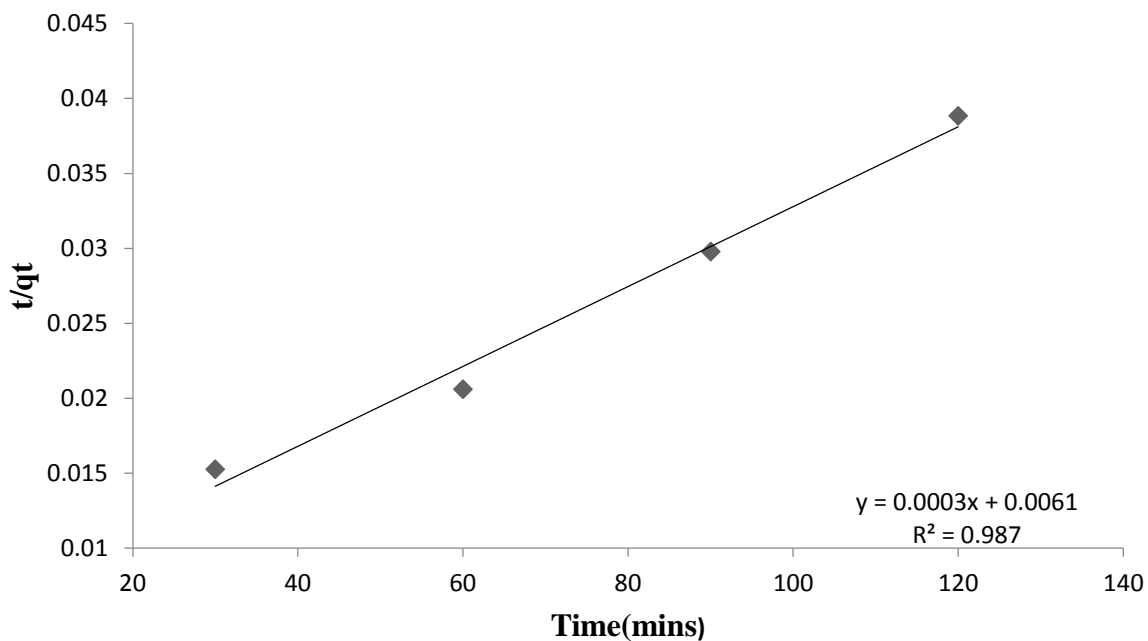


Fig. 7. Pseudo second order kinetics for the removal of DDVP from soil using APB

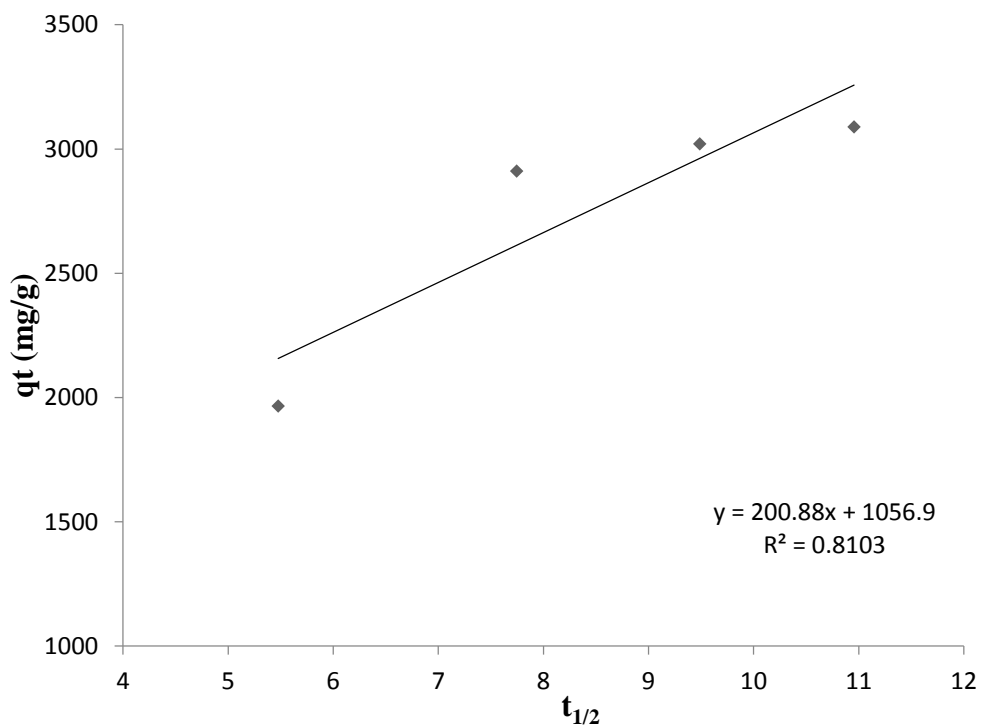


Fig. 8 Intra - particle diffusion kinetics for the removal of DDVP from soil using APB

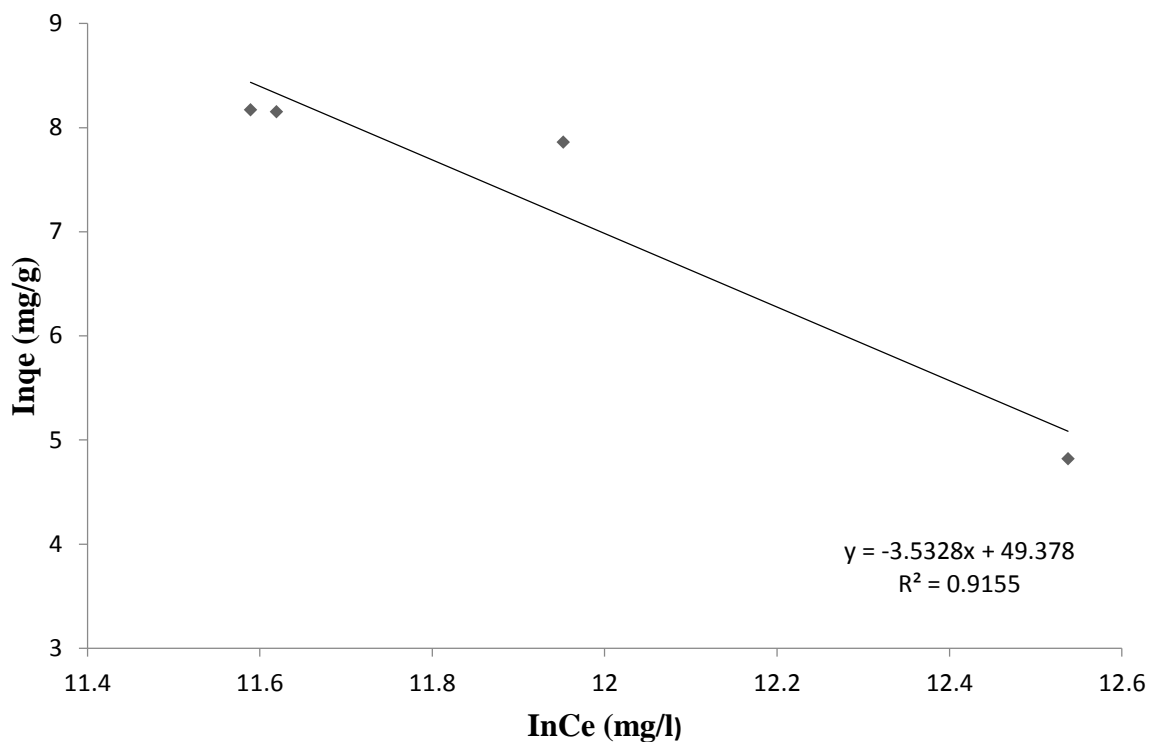


Fig. 9. Freundlich isotherm for the removal of DDVP from soil using APB

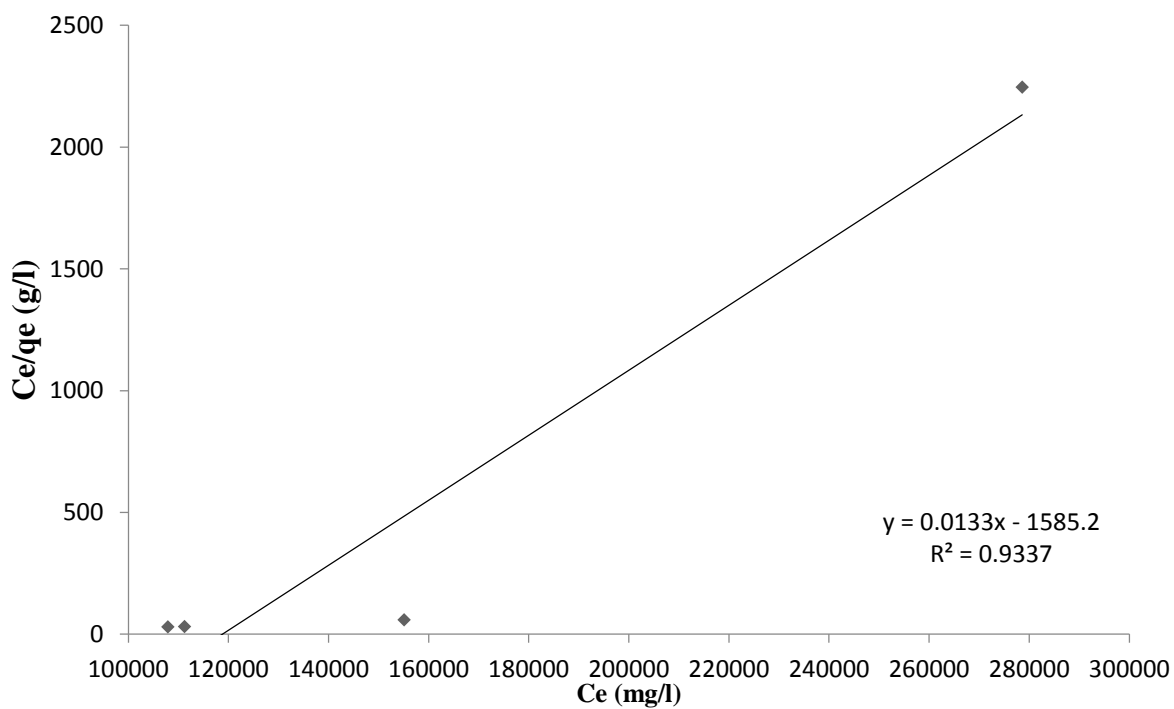


Fig. 10 Langmuir isotherm for the removal of DDVP from soil using APB

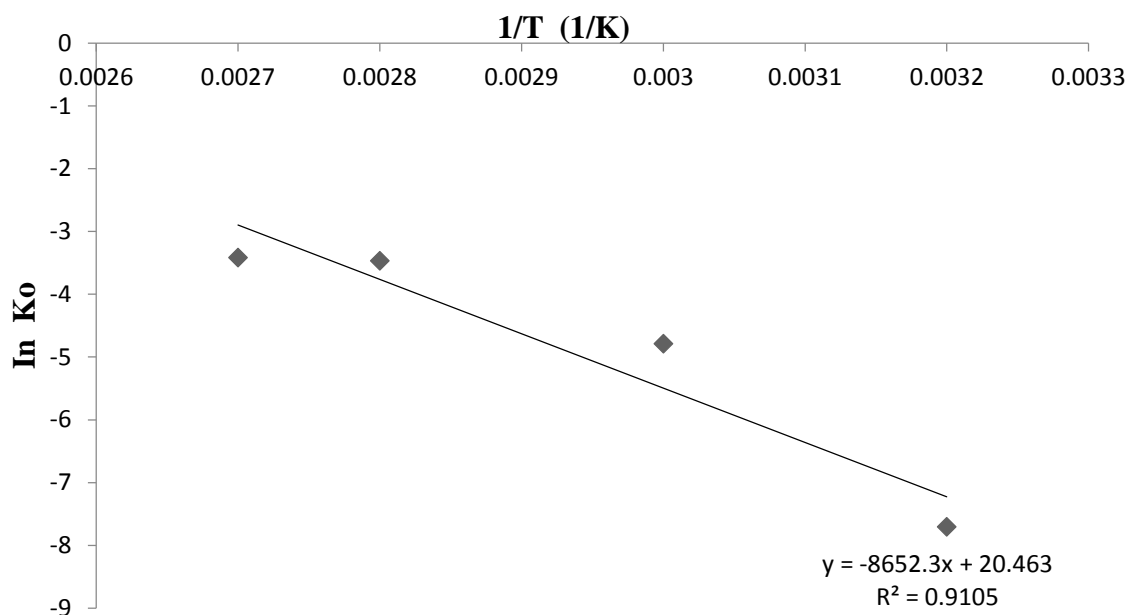


Fig. 11 Van't Hoff plot for the removal of DDVP from soil using APB

The effect of contact time on APB adsorption capacity is depicted in Table 1 and Figure 3 which showed that the adsorption of DDVP increased rapidly from 34.52% - 51.10% as the time increased from 30 minutes - 60 minutes and attained maximum saturation at about 120 minutes. Saturation of the adsorption sites onto the adsorbent was between 60-120 minutes (51.10% -54.25%) hence there was a slow increase in adsorption rate over time (Mane *et al.* 2007).

The adsorption of DDVP as shown in Table 3 and Figure 4, increased rapidly from 62.43% - 83.15% as the adsorbent dosage (ADP) increased from 2.0g - 2.5g. A gradual increase in adsorption rate was also observed from 90.91% - 95.65% as the dosage increased from 3.0g - 5.0g respectively. This was as a result of increased surface-area as well as the adsorption sites of DDVP molecules (Ozacar & Sengil, 2005; Rasoulifard *et al.* 2010).

Temperature was varied within 40°C, 60°C, 80°C and 100°C in other to review DDVP adsorption rate using APB. The adsorption of DDVP as shown in Table 3 and Figure 5, increased rapidly from 2.20% - 45.54% as temperature increased from 40°C - 60°C. A gradual increase in adsorption rate was also observed from 60.96% - 62.11% as the temperature increased from 80°C - 100°C respectively. This shows why the adsorbent and adsorbate ions had increased adsorptive interactions within their active sites (Dogan & Alkan, 2003).

In the kinetic study of the removal of DDVP from APB, three adsorption kinetics models were chosen. They are Lagergren pseudo-first order kinetic, pseudo second order kinetics and Intra - particle diffusion model presented in Figures 6 - 8. The linear plot/equation and correlation factors (R^2) for each of the models are indicated in Figures 6- 8. Figure 6 shows the correlation factor for Lagergren pseudo first order kinetics model to be nil and therefore indicates the worst fit. Intra - particle diffusion model presented in Figure 7 had a correlation factor of 0.8103 which seems low. Pseudo second order kinetics model had correlation factor of 0.987 which is closest to one and hence best illustrates the effect of contact time on DDVP using APB and is in agreement with Liu *et al.* (2007).

Freundlich and Langmuir isothermal models for the adsorption of DDVP using APB

Freundlich and Langmuir isothermal parameters for the adsorption of DDVP from soil using APB are shown in Table 4 while Figure 9 shows the Freundlich adsorption isotherm of DDVP using APB as adsorbent. The correlation factor shown in Table 5, $R^2 = 0.9155$ being close to 1 indicates a very good fit to the Freundlich adsorption isothermal model. Adsorption was compared using the slope $1/n$, which indicates whether adsorption is favoured. The value for $1/n$, (0.3) indicates that DDVP was favorably adsorbed using APB adsorbent and this is in accordance to Gupta *et al.* 2007 in their study on adsorption kinetics and thermodynamics of

organophosphorus profenofos pesticide onto Fe/Ni bimetallic nanoparticles. Figure 10 shows the Langmuir adsorption isothermal model for DDVP removal using APB as adsorbent. As presented in Figure 10 the Langmuir model fits quite well with the experimental data ($R^2 = 0.9337$). The correlation factor being close to 1 indicates a very good fit to the Langmuir adsorption isothermal model. The value of R_L (0.003) reveals that DDVP adsorption using APB was favorable. In accordance to Hall (1966), the Langmuir model may fit the experimental data well due to the homogeneous distribution of active sites on APB surface.

Van't Hoff plot for the adsorption of DDVP using APB

Table 6 shows the Adsorption kinetics parameters for the adsorption of DDVP using APB. Figure 11 shows the Van't hof plot for the adsorption of DDVP using APB as the adsorbent. The observed thermodynamic values are listed in Table 7. ΔG° had positive values of 2196.18, 1452.45, 1114.23 and 1160.69 at temperature of 40°C, 60°C, 80°C and 100°C respectively. All positive values for ΔG° indicate the non-spontaneous nature of adsorption of DDVP. The positive value of ΔS° (18.6316) indicates the increased randomness at the solid-solution interfaces during adsorption as is in agreement with Mansourieh, *et al.* (2016) in their study on adsorption kinetic and thermodynamics of organophosphorus profenofos pesticide onto Fe/Ni bimetallic nanoparticles. The positive value of ΔH° (7877.92) indicates the endothermic nature of the adsorption.

IV. CONCLUSION

This study showed that APB has the potential as an adsorbent in quantitative removal of DDVP from soil. Graphical illustrations revealed that the percentage removal of DDVP increased at different interval of time, dosage and temperature. The equilibrium data for Langmuir and Freundlich models of adsorption were well-fitted thereby indicating both monolayer and multilayer coverage of DDVP molecules on APB. Thermodynamic parameters (Van't hof plot) indicate a non-spontaneous and endothermic process. The results attained by comparison of kinetic models for the adsorption system followed the pseudo-second-order kinetic model. Also, minimization of voluminous waste biomass to yield biochar production through pyrolytic process provides means to solve the problem of management and disposal of waste biomass in the environment.

REFERENCES

- [1]. Azargohar, R., & Dalai, A. K. (2006). Biochar as a precursor of activated carbon. *Applied Biochemistry and Biotechnology*, 131, (3), 762- 773.
- [2]. Bridgwater, A., V. (2003). Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal*, 91, (3), 87-102.
- [3]. Dogan M. & Alkan M (2003) Adsorption kinetics of methyl violet on topersilite. *Chemosphere* 50:517-528
- [4]. Goldberg, E. D. (1985). Black carbon in the environment: properties and distribution. ISBN 0471819794, New York, USA.
- [5]. Hall, K.R. (1966). Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. *Ind. Engng Chem. Fundam.*
- [6]. Hagner, M. (2016). Maaseudun tulevaisuus. Retrieved December 2, 2016, from <http://www.maaseuduntulevaisuus>.
- [7]. Komang, R., and Orr, C. (2016). Biochar application: Essential soil microbial ecology. Elsevier Science and Technology Books, 21 (4), 76-89.
- [8]. Kuhlbusch, T.A., and Crutzen, P.J. (1995). Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO₂ and a source of O₂. *Global Biogeochemistry Cycles*, 9: 491-501.
- [9]. Lehmann, J., Gaunt, J., and Rondon, M. (2006). Biochar sequestration in terrestrial ecosystems. *Mitigation and Adaptation Strategies for Global Change*, 11, (2), 403-427.
- [10]. Liu, Y., Xiao, D., & Li, H. (2007). Kinetics and thermodynamics of Lead (II) adsorption on vermiculite. *Separation. Science and Technology*, 42, 185-202
- [11]. Mane VS, Mall ID, Srivastava VC (2007) Use of bagasse fly ash as an adsorbent for removal of brilliant green dye from aqueous solution. *Dyes Pigm* 73:269-278.
- [12]. Mansourieh, N., Sohrabi, M. R., Khosravi, M. (2016). Adsorption kinetics and thermodynamics of organophosphorus profenofos pesticide onto Fe/Ni bimetallic nanoparticles. *Islamic Azad University (IAU)*.
- [13]. Mench, M., Lepp, N., Bert, V., Schwitzguebel, J. P., Gawronski, S.W., Schöder, P. (2010). Successes and limitations of phytotechnologies at field scale, *Journal of Soils and Sediments*, 10 (6), 1039-1070.
- [14]. Ozacar M, Sengil IA (2005). Adsorption of metal complex dyes from aqueous solutions by pine sawdust. *Bioresour Technol* 96:791-795
- [15]. Özçimen, D., and Karaosmanoğlu, F. (2004). Production and characterization of bio-oil and biochar from rapeseed cake. *Renewable Energy*, 29 (5).
- [16]. Powlson, D. S., Whitmore, A. P., & Goulding, K. W. (2011). Soil carbon sequestration to mitigate climate change: a critical re-examination to identify the true and the false. *European journal of soil science*, 62(1), 42-55.
- [17]. Powlson, D. S., Whitmore, A. P., & Goulding, K. W. (2011). Soil carbon sequestration to mitigate climate change: a critical re-examination to identify the true and the false. *European journal of soil science*, 62(1), 42-55.
- [18]. Rasoulifard, M. H., Esfahani, F. H., Mehrizadeh, H., Sehati, N. (2010). Removal of C.I. Basic Yellow 2 from aqueous solution by low-cost adsorbent: Hardened paste of Portland cement. *Environmental Technology*. 31(3):277-84.
- [19]. Schmidt, H. P., Kammann, C., Niggli, C., Evangelou, M. W., Mackie, K. A., & Abiven, S. (2014). Biochar and biochar-compost as soil amendments to a vineyard soil: Influences on plant growth, nutrient uptake, plant health and grape quality. *Agriculture, Ecosystems & Environment*, 191, 117-123.
- [20]. Sohi, S. P., Krull, E., Lopez-Capel, E., & Bol, R. (2010). A review of biochar and its use and function in soil. *Advances in agronomy*, 105, 47-82.

- [21]. Vangronsveld, J., Herzig, R., Weyens, N., Boulet, J., Adriaensen, K., Ruttens, A., & Mench, M.(2009). Phytoremediation of contaminated soils and groundwater: lessons from the field. *Environmental Science and Pollution Research*, 16, 765-794.
- [22]. Wayne, T., S. (2012). Capturing Heat from a Batch Biochar Production System for Use in Greenhouses and Hoop Houses. *Journal of Agricultural Science and Technology. A*, 2(12A), 1332.
- [23]. Yang, Y., & Sheng, G. (2003). Enhanced pesticide sorption by soils containing particulate matter from crop residue burns. *Environmental science & technology*, 37(16), 3635-3639.
- [24]. Zhou, Q., & Song, Y. (2004). *Contaminated soil remediation: principles and methods*. Science Press, Beijing, Google Scholar.