Adsorption Of 2, 3-Dichlorovinyl Dimethyl Phosphate (DDVP) From Aqueous Solution Onto Groundnut Shell Activated Carbon: Isotherm And Kinetic Studies

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Abstract: In this research, groundnut shell, was used to produce low-cost adsorbents for the removal of 2, 3-dichlorovinyl dimethyl phosphate (DDVP) in aqueous solution. The one step activation process was adopted, using three activating agents: phosphoric acid, potassium carbonate and nitric acid. The raw groundnut shell along side with the different activated carbon produced were subjected to different analysis: physico-chemical, scanning electron microscopy (SEM), methylene blue and Iodine number as well as a determination of the ability of these samples to adsorb DDVP in aqueous solution. The methylene blue and Iodine number gave strong indication of the activated carbon to have good potentials of its use as adsorbent, having both microporous and mesoporous structures, hence meeting the minimal requirement for the purpose. The SEM analysis showed morphologies of the samples indicating activated carbon that is heterogeneous in nature (i.e consisting of both micropore and mesopore structures). The study concludes that groundnut shell is a very good precursor for use as adsorbents which can be incorporated for adsorption of DDVP from aqueous solutions. This method will be highly rewarding in converting waste to wealth, contributing in having cheaper sources of adsorbent and as well getting rid of solid wastes from the environment, serving as a beneficial solid waste management technique.

Keywords: Groundnut shell, DDVP, Activation, Adsorption Isotherms/Kinetics

I.   INTRODUCTION

Activated carbon is a highly porous and adsorbent material. It is applied in domestic, commercial and industrial settings (Mendez *et al.*, 2006). In the food industry, activated carbon is used in decolourization, deodorization and for taste removal. It is also used to remove heavy metals and organic contaminants from liquids. In medicine, it is used for adsorption of harmful chemicals and drugs (Oyo & Igbokwe, 2001; Innamullah *et al.*, 2008). Basically, there are two different processes for the preparation of activated carbon: the physical or thermal and chemical activation. The physical activation involves subjecting the material to high temperatures of between 700°C and 1000°C using air, carbondioxide or water vapour. The chemical activation involves the use of activating agents such as phosphoric acid, sodium hydroxide, potassium hydroxide, zinc chloride, etc. In chemical activation, the raw material or carbonized sample is impregnated with an activating agent and then heated in a furnace. Activated carbon is the most widely known and used adsorbent (a material that has the ability to extract certain substances from gases, liquids or solids, causing them to

adhere to its surface without changing its properties) but it is highly expensive. There has been urgent need for cheaper sources of adsorbents. The non- conventional sources from food waste have been identified as alternatives to the expensive activated carbon (Abdul & Aberuagba, 2005).

In the present work, more attention is focused on the effective use of domestic agricultural by-products being widely distributed in Nigeria in order to reduce the huge sums of money used in importing the commercial activated carbon. In this study, groundnut shell is used to prepare activated carbon using the chemical activation method.

Adsorption is the phenomenon of accumulation of large number of molecular species at the surface of liquid or solid phase in comparison to the bulk. The process of adsorption arises due to presence of unbalanced or residual forces at the surface of liquid or solid phase. These unbalanced residual forces have tendency to attract and retain the molecular species with which it comes in contact with the surface. Adsorption, essentially a surface phenomenon, is a term which is completely different from absorption .While absorption means uniform distribution of the substance throughout the bulk, adsorption essentially happens at the surface of the substance. When both Adsorption and Absorption processes take place simultaneously, the process is called Sorption. Adsorption process involves two components, adsorbent and adsorbate. Adsorbent is the substance on the surface of which adsorption takes place. Adsorbate is the substance which is being adsorbed on the surface of adsorbent. Adsorbate gets adsorbed.

Adsorbate + Adsorbent = Adsorption

Adsorption can also be defined as the adhesion of atoms, ions, or molecules from a gas, liquid, or a dissolved solid to a surface. This process creates a film of the adsorbate to the surface of the adsorbent. This process differs from absorption. Adsorption is a surface-based process while absorption involves the whole volume of the material. Adsorption is present in many physical, biological, and chemical systems, and is widely used in industrial applications such as the use of activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increase storage capacity of carbide-derived carbons, and water purification (Nwufo & Ezeoma, 1995). Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Lesser known are the pharmaceutical industry applications as a means to prolong neurological exposure to specific drugs or parts thereof.

A very large amount of water can be adsorbed by the "internal" surfaces of the grains in the pile of sand, and this absorption is simply "internal adsorption. If water is made to flow through such a pile of sand, ions and toxins it may be preferentially adsorbed by the surfaces of the grains of sand, providing a simple, well-known water purification application.
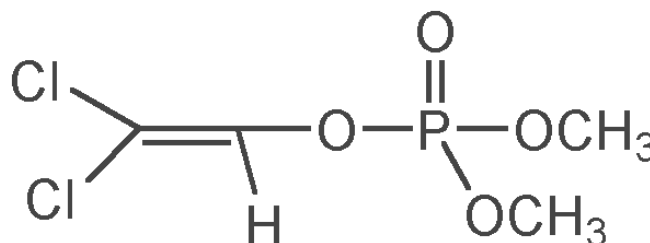

Figure 1.1: DDVP Structure

Dichlorvos (2, 3-dichlorovinyl dimethyl phosphate) (Fig.1.1) is one of the classes of insecticides referred to as organophosphates used to control households and stored products insects. It is effective against mushroom flies, aphids, spider mites, caterpillars, and white flies in greenhouse, outdoor fruits, and vegetable crops (Lotti, 2001). Therapeutically, dichlorvos is used as a fumigant or to treat a variety of parasitic worm infections in dogs, livestock and humans. It acts against insects as both a contact and a stomach poison (Lotti, 2001). Dichlorvos pesticide self-poisoning is an important clinical problem in the developing world, and kills an estimated 200 000 people every year (Michael *et al*., 2008). Concentrates of dichlorvos is mildly irritating to skin and may cause localized sweating, involuntary muscle contractions and burning sensations or actual burns (Aaron, 2001). When inhaled, the first effect is usually respiratory one and may include bloody or runny nose, coughing, chest discomfort, difficult or short breath, and wheezing due to constriction or excess fluid in the bronchial tubes. Eye contact will cause pain, bleeding, tears, pupil constriction, and blurred vision. Following exposure by any route, other systemic effects may begin within a few minutes or be delayed for up to 12 hours. These may include pallor, nausea, vomiting, diarrhoea, abdominal cramps, headache, dizziness, eye pain, blurred vision, constriction or dilation of the eye pupils, tears, salivation, sweating, and confusion. Severe poisoning will affect the central nervous system, producing in-coordination, slurred speech, loss of reflexes, weakness, fatigue, involuntary muscle contractions, twitching, tremors of the tongue or eyelids, and eventually paralysis of the body extremities and the respiratory muscles. In severe cases there may also be involuntary defecation or urination, psychosis, irregular heartbeats, unconsciousness, convulsion and coma. Death may be caused by respiratory failure or cardiac arrest (Michael *et al*., 2008). Repeated or prolonged exposure to dichlorvos may result in the same effects as acute exposure including the delayed symptoms. Other effects may include impaired memory and concentration, disorientation, severe depressions, irritability, confusion, headache, speech difficulties, delayed reaction times, nightmares, sleepwalking and drowsiness or insomnia. An influenza-like condition with headache, nausea, weakness, loss of appetite, and malaise has also been reported (Clark, 2002; Michael *et al*., 2008).

In Nigeria, especially the northern part, dichlorvors is traded under different names such as Nuvan, Sniper, Pia-pia (Hausa) and is handled and used as a household insecticide indiscriminately.

The aim of this study is to produce activated carbon from groundnut shell for use as adsorbent for the purpose of removing DDVP and its residue from aqueous solution.

II. MATERIALS AND METHODS

Groundnut shell was collected from local farmers in Keffi, Nasarawa State during harvest. The sample Groundnut shell (GS). It was washed thoroughly with water to remove all surface impurities, after which it was sun-dried. The sun-dried samples was then ground with mortar and pestle and sieved with a 2mm mesh size sieve and then further dried in an oven overnight.

Selected pesticide, 2, 3-dichlorovinyl dimethyl phosphate (DDVP), was purchased from designated shops for use in the research as adsorbate. It is also the pesticide commonly used in the home as insecticide. The analysis was carried out at the Laboratory Complex of Federal Ministry of Agriculture, Abuja road, Kaduna.

A. REAGENTS, CHEMICALS AND INSTRUMENTS

All reagents and chemicals that were used are of analytical grade. Distilled water was used all through for the preparation of standard solutions. All equipment and apparatus used were standardized to specification.

B. PREPARATION OF ACTIVATED CARBON FROM THE SAMPLES

The one-step activation process of adsorbent production was adopted. In this method, groundnut shell, was activated separately by mixing each with standard solutions of H_3PO_4, K_2CO_3, and HNO_3, respectively in the ratio of 1:1 (i.e. 1g of sample to 1ml of activating agent) and allowed to stand for 24 hours (Gimba, *et al*. 2004).

The sample was transferred into crucibles and loaded into a muffle furnace to attain a temperature of 600^oC and maintained for 2h. The samples were allowed to cool to room temperature and then washed separately with 0.1MHCl to remove surface ash and further rinsed with distilled water to remove residual acid. Washing is said to be completed when pH of 6 to 8 is achieved. Each of the samples was dried in an oven at 105^0C to remove the moisture in it. The different adsorbents produced from the 3 samples using the 3 different activating agents were stored in a desiccator for subsequent analysis.

C. CHARACTERIZATION OF THE ACTIVATED CARBON

Moisture content, ash content, bulk density and pH were all determined using standard methods. Preliminary studies were also carried out on the produced activated carbon by determination of methylene blue number, Iodine content and Scanning electron microscopy (SEM).

D. EFFECT OF INITIAL CONCENTRATION AND CONTACT TIME

In order to determine the equilibrium time for maximum DDVP uptake, different concentrations of DDVP (5, 10, 15, 20 and 25 mg/l) and contact time were used for adsorption. 1g of each of the activated carbons produced ($GSAC_x$, $GSAC_y$ and $GSAC_z$), was added into 100ml of the different concentrations of the adsorbate and shaken in a flask shaker at 150 rpm for different time ranges (10, 20, 30, 40, 50, 60, 70, 80 and 90 min). After each time range, the mixture was quickly filtered and the absorbance of the filtrate was determined using UV/Visible spectrophotometer at 232nm.

The absorbance readings of the filtrate were compared with the calibration curve of the DDVP and the concentration of each filtrate at each time interval was determined.

The concentration of DDVP adsorbed by the adsorbent, C_{ad} (initial concentration- concentration of filtrate), and adsorption capacity, q_e, were calculated.

Adsorption capacity$(q) = (C_0 - C_f) * v/w$
C_0 – initial concentration in mg/l
C_f – final concentration from sample in mg/l
q- adsorption capacity in mg/g
v- volume in litre
w- weight of the activated carbon in g

E. ADSORPTION ISOTHERM AND KINETIC STUDIES

Adsorption Isothermic studies for Freundlich, Langmuir and Temkin models as well as pseudo-first and pseudo-second order kinetic models were investigated (Njoku, *et al*. 2015).

III. RESULTS AND DISCUSSIONS

Three different activated carbons were from groundnut shell using three activating agents and labeled $GSAC_x$ (from phosphoric acid), $GSAC_y$ (from potassium carbonate) and $GSAC_z$ (from nitric acid). The raw groundnut shell sample is labeled GS. The moisture content and bulk densities of the raw and activated carbon produced from groundnut shell all meet the requirements of being good precursors of adsorbents (Malik *et al*. 2006), (Table 3.1) The methylene blue number of $GSAC_x$ and $GSAC_z$ are 119 and 111 respectively(Table 3.2). This indicates also that the activated carbon has mesoporous structure. All activated carbon with MBN of 100 and above are said to be good adsorbents. The iodine value (Table 3.3) showed that all the activated carbon meet the specification for good adsorbents, having Iodine number of between 300-1200 (Etonihu, *et al*. 2011). The $GSAC_y$ has the highest iodine number, suggesting that its morphology is more microporous than the others. From the SEM morphology (plate I-IV), it is clear that all the activated carbon produced show a mixture of micropores and mesopores, agreeing with the preliminary analysis of iodine and methylene blue number results. $GSAC_x$ showed the best pore distribution morphology.

S/NO	Sample	Moisture Content %	Ash Content %	pH	Bulk density g/cm³
1	GS	4.2	6.0	6.37	0.244
2	$GSAC_x$	4.7	-	6.7	0.451
3	$GSAC_y$	4.8	-	6.8	0.455
4	$GSAC_z$	4.7	-	6.6	0.452

Table 3.1: Physico-Chemical Parameters of the Samples

S/N	Sample	Methylene blue number (MBN)
1	$GSAC_x$	119
2	$GSAC_y$	66
3	$GSAC_z$	111

Table 3.2 Methylene Blue Number (MBN) of the Activated Carbon

S/N	Sample	Iodine value
1	GS	889
2	$GSAC_x$	508
3	$GSAC_y$	931
4	$GSAC_z$	550

Table 3.3: Iodine Value Determination for Raw and Activated Samples

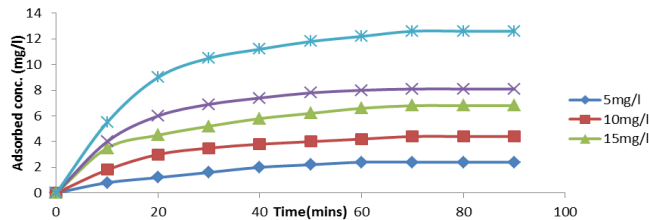## ADSORPTION OF ADSORBATE (DDVP) BY ACTIVATED CARBONS (ADSORBENTS) PRODUCED

Figure 3.1: Plot of adsorbed concentrations from initial concentrations of DDVP on GS at different contact time

C0	Ce	ln Ce	qe	ln qe	Ce/qe
5	2.4	0.8755	0.26	-1.3471	9.23
10	4.4	1.4816	0.56	-0.5798	7.86
15	6.8	1.9169	0.82	-0.1985	8.29
20	8.1	2.0919	1.19	-0.0845	6.81
25	12.6	2.5337	1.24	0.2151	10.16

Table 3.4: Adsorption data for different DDVP concentrations on groundnut shell (GS) at equilibrium time
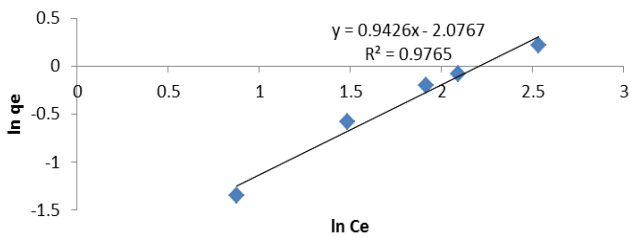
Figure 3.Ia: Freundlich adsorption Isotherm of DDVP on groundnut shell (GS)
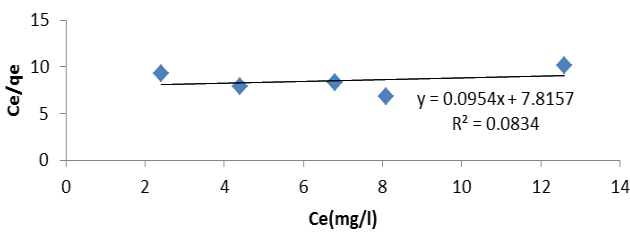
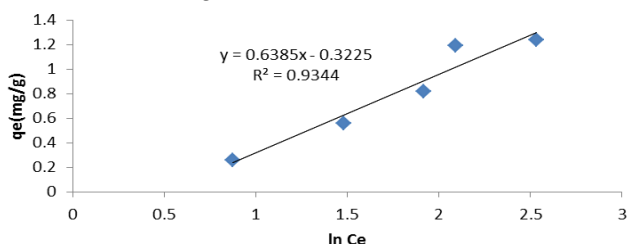*Figure 3.Ib: Langmuir Adsorption Isotherm of DDVP on groundnut shell (GS)*

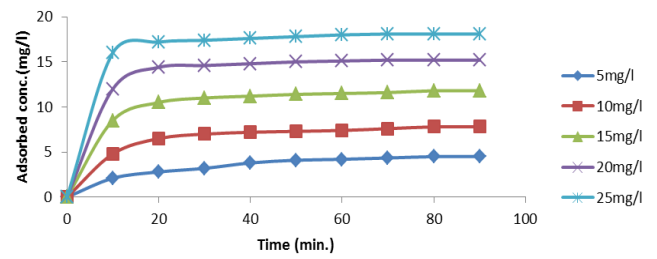*Figure 3.Ic: Temkin Adsorption Isotherm of DDVP on groundnut shell (GS)*

Figure 3.II: Plot of adsorbed concentrations from initial concentrations of DDVP on $GSAC_x$ at different contact time

C_0	C_e	$\ln C_e$	q_e	$\ln q_e$	C_e/q_e
5	0.5	-0.6931	0.45	-0.7985	1.11
10	2.2	0.7885	0.78	-0.2485	2.82
15	3.2	1.1632	1.18	0.1655	2.71
20	4.8	1.5686	1.52	0.4187	3.16
25	6.9	1.9315	1.81	0.5933	3.81

Table 3.5: Adsorption data for different DDVP concentrations on groundnut shell activated using phosphoric acid as activating agent ($GSAC_x$) at equilibrium time
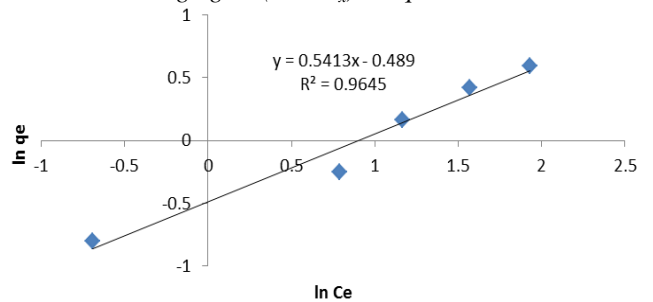

Figure 3.IIa: Freundlich adsorption Isotherm of DDVP on groundnut shell activated using phosphoric acid as activating agent ($GSAC_x$)
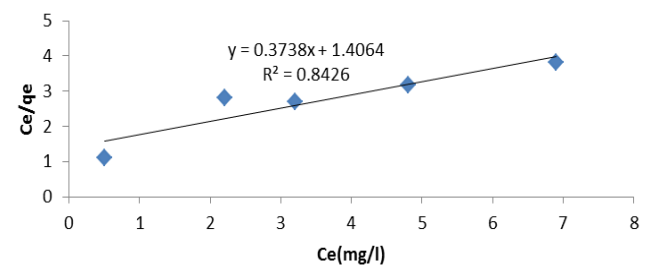

Figure 3.IIb: Langmuir Adsorption Isotherm of DDVP on groundnut shell activated using phosphoric acid as activating agent ($GSAC_x$)
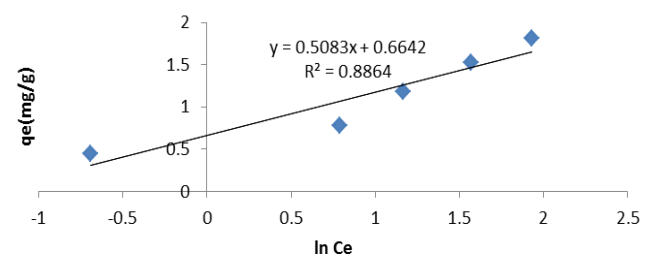

Figure 3.IIc: Temkin Adsorption Isotherm of DDVP on groundnut shell activated using phosphoric acid as activating agent ($GSAC_x$)

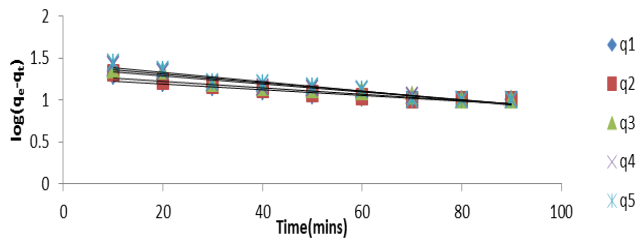## PSEUDO FIRST ORDER KINETIC MODELS

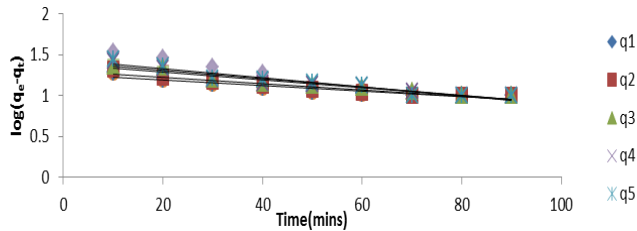*Figure 3.V: Pseudo- first-order kinetics for the adsorption of DDVP onto GS*

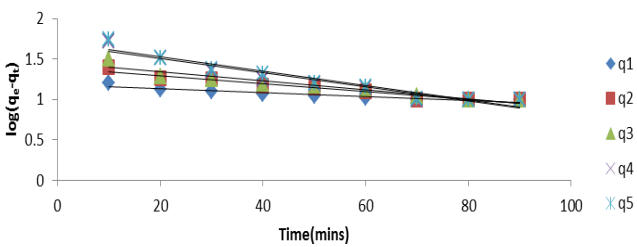*Figure 3.Va: Pseudo- first-order kinetics for the adsorption of DDVP onto $GSAC_x$*

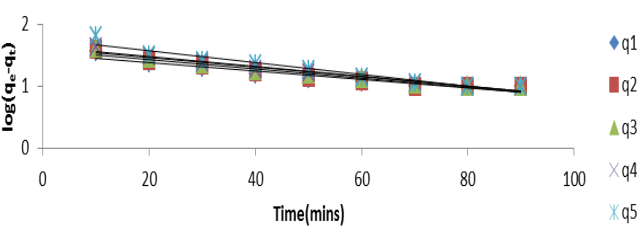*Figure 3.Vb: Pseudo- first-order kinetics for the adsorption of DDVP onto $GSAC_y$*

Figure 3.Vc: Pseudo- first-order kinetics for the adsorption of DDVP onto $GSAC_z$

Sample	R^2	Slope	Intercept	Rate constant(k_1)	$q_{e, cal}$	$q_{e, exp}$
GS	0.919	0.005	1.444	0.012	27.80	1.26
GSACx	0.925	0.007	1.563	0.016	36.56	1.81
GSACy	0.929	0.009	1.707	0.021	50.90	1.90
GSACz	0.923	0.009	1.761	0.021	57.68	1.95
CAC	0.982	0.023	3.067	0.053	116.87	1.66

Table 3.8: Results of Pseudo-first-order kinetic model for raw samples and activated carbon

From the experimental data, the pseudo-first order kinetic models show that R^2 is high, but the amounts adsorbed at equilibrium, $q_{e, cal}$ do not agree with same from the experiment (Njoku, *et al*. 2015). This shows that the data does not fit into the pseudo- first order kinetic model.

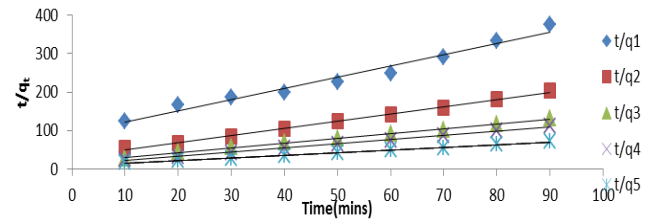## PSEUDO SECOND ORDER KINETIC MODELS

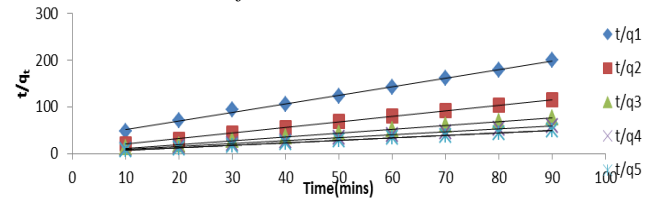*Figure 3.VI: Pseudo- second-order kinetics for the adsorption of DDVP onto GS*

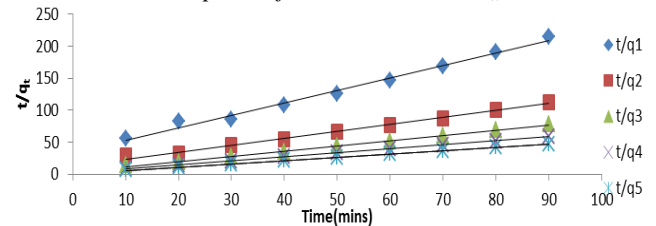*Figure 3.Via: Pseudo- second-order kinetics for the adsorption of DDVP onto $GSAC_x$*

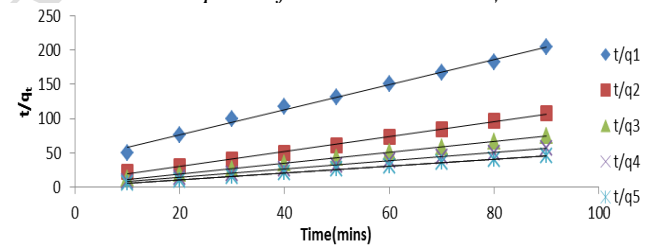*Figure 3.VIb: Pseudo- second-order kinetics for the adsorption of DDVP onto $GSAC_y$*

Figure 3.Vic: Pseudo- second-order kinetics for the adsorption of DDVP onto $GSAC_z$

Sample	R^2	Slope	Intercept	Rate constant(k_2)	$q_{e, cal}$	$q_{e, exp}$
GS	0.996	0.673	9.282	0.049	1.486	1.26
GSACx	0.999	0.541	0.895	0.327	1.848	1.81
GSACy	0.999	0.512	1.024	0.256	1.953	1.90
GSACz	0.999	0.498	1.087	0.228	2.008	1.95
CAC	0.999	0.561	3.355	0.094	1.783	1.66

Table 3.9: Results of Pseudo-second-order kinetic model for raw samples and activated carbon

From the experimental data, the pseudo-second order kinetic models show that R^2 is high, 0.99 and the amounts adsorbed at equilibrium, $q_{e, cal}$ do agree with the amount adsorbed at equilibrium from the experiment, $q_{e, exp}$. This shows that the data fits well into the pseudo- second order kinetic model. Very high values of R^2 in addition to agreement of q_e obtained from the models and the experimental values are used in confirming the suitability of the models in fitting the kinetic data. A better fit to the pseudo- second order model suggests that the adsorption rate is dependent more on the availability of adsorption sites than the concentration of the DDVP in solution (i.e. the adsorption depends on the

availability of sites on the activated carbon rather than the concentration of the pesticide).

IV. CONCLUSION

This study indicates that groundnut shell activated carbon could be used as efficient adsorbent for the removal of DDVP from aqueous solution. It is also found that the equilibrium data fitted well with Freundlich adsorption model with correlation coefficient near to unity and adequate binding force. Kinetic studies also revealed that the data fits well into the pseudo-second order kinetic model. Groundnut shell is therefore, a good precursor for use as an adsorbent that can be utilized for the removal of DDVP in contaminated aqueous solutions.

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