

Adsorption of Dichlorvos in aqueous solution onto Activated Carbon from *Canarium Schweinfurthii* Seed Shell

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Abstract— Activated carbons were prepared from the agricultural waste *Canarium schweinfurthii* seed shell with zinc chloride ($ZnCl_2$) and Phosphoric acid (H_3PO_4) as chemical activation agents. The activated carbons were prepared by carbonization at 300°C, 350°C, 400°C, 450°C and 500°C for 5, 10 and 15 minutes. The optimum conditions for activated carbon production were evaluated based on the determination of adsorption capacity of Dichlorvos. It was found that the maximum unit capacity for Dichlorvos was 39.42 mg/g at activation temperature of 300°C and activation time of 5 minutes with zinc chloride as the activating agent. It was found that the optimum unit capacity for Dichlorvos was 39.08 mg/g at activation temperature of 300°C and activation time of 5 minutes using Phosphoric acid as activating agent. This study showed that both activated carbons produced with zinc chloride and phosphoric acid as activating agent can be utilized as effective matrices for Dichlorvos removal from aqueous medium.

Index Terms— Activated carbon, Adsorption, Agricultural wastes, *Canarium Schweinfurthii*, Dichlorvos

1 INTRODUCTION

Carbon material with high porosity and high surface area are called activated carbons which are manufactured from coal [1], [2]. Agriculture wastes are a few examples of lignocellulosic precursor for activated carbon production.

Generally, the manufacture of activated carbon involves two main steps: the carbonization of the carbonaceous raw material below 1073K in the absence of oxygen and the activation of the carbonized product. In the chemical activation process, these two steps are carried out simultaneously using chemical activating agent as dehydrating agents and oxidants [3]. The physical activation, on the other hand, involves carbonization of a carbonaceous precursor followed by the activation of the resulting char at elevated temperature in the presence of steam or carbon dioxide. The temperatures used in the chemical activation are lower than those used in the physical activation. Therefore, the development of a porous structure within the carbonaceous materials is enhanced using the chemical activation; this is due to the ability of the chemical agent to inhibit the formation of tar [4]. Among the chemical activating agents, zinc chloride in particular is the most widely used chemical in the preparation of activated carbon [3].

Pesticides have been used in agriculture throughout the recent decades to improve the efficiency of food production but adverse effect of its intensive use have resulted in the ubiquitous presence of pesticide residue in surface water [5].

Dichlorvos (2,2-dichlorovinyl dimethylphosphate) or DDVP is a highly volatile organophosphate, widely used as a fumigant to control household pest in public health, and protecting stored products from insects. It is effective against mushroom, flies, aphids, spider mites, caterpillars etc in greenhouse outdoor fruit and vegetable crops; also it is used in the milling and grain handling industries. It acts against insects both as contact and stomach poison. There is a major concern over its acute and chronic toxicity [6].

Many studies tailored towards the solution of this problem involve determination of adsorption of pesticides on various adsorbents such as bentonite, kerolite and zeolite [7]. Activated carbon materials have a special place among these adsorbents, as for a long time they are known to be capable of adsorbing various organic compounds and in recent years the number of studies on adsorption of pesticides on carbon materials from aqueous solution have increased [8]. Adsorption by activated carbon (AC) has been successfully used in wastewater and drinking water treatment plants to remove different pollutants such as surfactants, pesticides, dyes, and aromatic compounds [9].

Canarium schweinfurthii seed shell is very cheap and readily available in the Middle Belt region of Nigeria; studies on the utilization of *Canarium schweinfurthii* seed shell as a precursor for manufacturing activated carbon are minimal or not yet reported. In addition, information concerning the adsorption of Dichlorvos onto *canarium schweinfurthii* seed shell has not been reported. Therefore, the aim of this study is to describe the feasibility of the preparation of activated carbon from the agricultural waste, *Canarium schweinfurthii* seed shell by chemical activation and to investigate the adsorption capacity of the prepared activated carbon on the adsorption of Dichlorvos in aqueous solution. The significance of this study is channeled towards optimizing the preparation condition of Activated carbon using *Canarium schweinfurthii* and the viability of using *Canarium schweinfurthii* based activated carbon for reclaiming wastewater polluted with pesticides.

2 MATERIALS AND METHODS

2.1 Preparation of Adsorbent

In the present study, *Canarium schweinfurthii* seed shell was used for the preparation of activated carbon. The seeds were

washed and sundried then crushed using a jaw crusher into smaller particle sizes. They were further pulverized into fine granular form. The sample was sieved into a particle size of 850µm-1.18mm. The granular was carbonized at 250°C for 3 hours in an oven. The carbonized sample was subjected to chemical activation, by the addition of 1M ZnCl₂ and 1 M H₃PO₄ solutions separately. The sample was then activated in the furnace for 5, 10 and 15 minutes at 300°C, 350°C, 400°C, 450°C and 500°C. The activated carbon produced was washed with distilled water to remove the excess activating agent it was then oven dried at 120°C and stored in sealed air-tight polythene bags for the further study [10]. Electric shaker Griffin flask shaker, Vecstar Furnace model ECF2, K.H Huppert Oven model DR-OV, Micro processor pH meter HANNA Instrument pH 210, UV-Visible Spectrophotometer Thermospectronic Hehlos serial no 101505, Centrifuge Baird and Tatlock Auto Bench Centrifuge were used. All the chemicals used were of analytical reagent grade obtained from B.D.H and E.Merck except were stated.

2.2 Adsorbates

Dichlorvos stock solution (20.0 mg/L) was prepared in distilled water using Dichlorvos stock 100% w/v. The working solution was obtained by diluting the stock solution in distilled water.

2.3 Batch mode adsorption studies

Batch mode adsorption studies were carried out with 50 mg of the activated carbon and 10 ml of the stock solution 20 mg/L, agitated at 200rpm in a mechanical shaker at room temperature. The different granular activated carbons produced were allowed to equilibrate with constant initial concentration of carbofuran solution (C₀ = 20ppm) [10]. Because of enough confidence of approach to equilibrium, these solutions were allowed to be agitated for 1 hour. The adsorbate solution was separated from the adsorbent by centrifugation at 3000rpm. The supernatant was passed through glass bedded column to avoid the passage of the adsorbate. The Dichlorvos was estimated spectrophotometrically at 490 nm using Diphenylsemicarbazide [11].

The amount of Dichlorvos adsorbed per mass unit of granular activated carbon in equilibrium condition, Q_e, was calculated by Equation (1),

$$Q_e = \frac{V(C_o - C_e)}{M} \quad (1)$$

Where V is the volume of Dichlorvos solution; C₀ and C_e are the initial and equilibrium concentrations of the Dichlorvos solutions respectively in mg/L; M is the mass of the granular activated carbon in g the equation gives Q_e in mg Dichlorvos adsorbed per g granular activated carbon.

2.4 Spectroscopic Determination of Dichlorvos

From the prepared solution of 1 molar NaOH 1ml was added to the solution of Dichlorvos and was allowed to stand for 30 minutes for complete hydrolysis, after which 1ml of 0.05% w/v of diphenylsemicarbazide in ethanol was added. A wine-reddish monomethine dye was formed and the absorbance was measured within 20 minutes at 490nm using UV spectrophotometer.

3 RESULTS AND DISCUSSION

3.1 Characterization of Canarium schweinfurthii Seed Shell

The physical properties of Canarium schweinfurthii seed shell determined were: bulk density, moisture content, Ash content, dry matter content and pH using the methods reported by Allen [12]. The results are presented in Table 1, from the physical properties of the raw canarium schweinfurthii seed shells it was observed that it is a very good precursor for the generation of activated carbon.

TABLE 1
PHYSICO-CHEMICAL PROPERTIES OF RAW SAMPLE OF CANARIUM SCHWEINFURTHII AND CARBONIZED SAMPLE

Parameters	Raw sample
% Moisture	5.10
% Dry matter	81.0
% Ash Content	0.5
Bulk density (g/cm ³)	1.33
% Yield of carbon	18.56
<u>pH measurement</u>	
(i) Raw	4.93
(ii) Carbonized	9.0

3.2 Adsorption of Dichlorvos

The maximum wavelength of Dichlorvos was measured as 490 nm. The absorbance versus concentration data for Dichlorvos was treated by linear regression analysis with R² = 0.925 as shown in Fig 1. For all the experiments, the adsorption process was studied at room temperature and pH value about 9.0. Adsorption of the Dichlorvos at initial concentration (C₀= 20 ppm) i.e stock solution and amount of granulated activated carbon (m = 50 mg) were monitored spectrophotometrically

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by the procedure described above. Absorbance data of Dichlorvos were obtained during the adsorption process, and then absorbance data were converted into concentration data using the corresponding calibration plots. The adsorption capacities were plotted as a function of time in Figure 2 and 3, the results shows that the amount of Dichlorvos adsorbed onto the activated carbon increases with increased in temperature of activation.

3.3 Effect of activation temperatures

From the result presented on Figures 2 and 3, as the activation temperature increased there was no significant increase in the adsorption capacities. This may be due to the temperature stability and catalytic activity of zinc chloride [14]. Also the solubility of the Dichlorvos affects the adsorption capacity of the activated carbon, because pure carbon is hydrophobic [15]. From literature it was found that the pesticides with higher solubility were weaker adsorbates and showed lower removal efficiency and smaller adsorption capacity [16]. More also, there is an inverse relationship between the adsorption capacity and the temperature of activation, as the temperature of activation increases the amount of Dichlorvos adsorbed decreases, this shows that Dichlorvos is adsorbed onto activated carbon with micro pores and the distribution of the pores also account for these inverse adsorption with temperature increase [17].

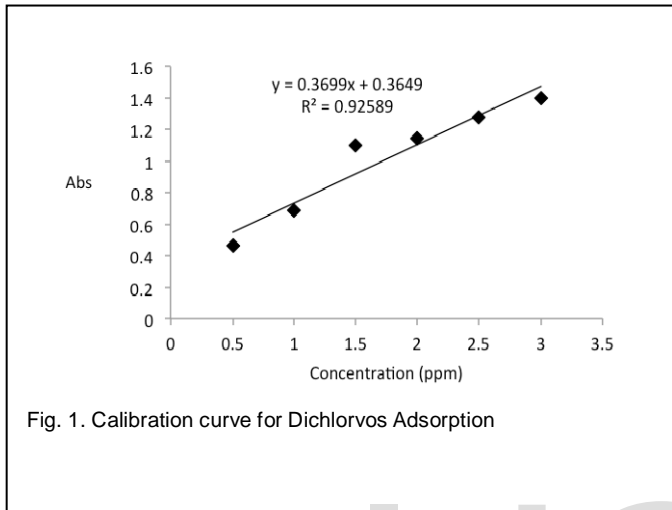


Fig. 1. Calibration curve for Dichlorvos Adsorption

3.3 Effect of activation time

Figure 2 and 3 represent the amount of dichlorvos adsorbed onto activated carbon from *Canarium Schweinfurthii* seed shell with zinc chloride and Phosphoric acid, the result shows a linear relationship between the adsorption capacity and the time of activation. Dichlorvos adsorption involves high energy binding sites on the activated carbon, as the temperature of activation increases with time, the higher energy site are satu-

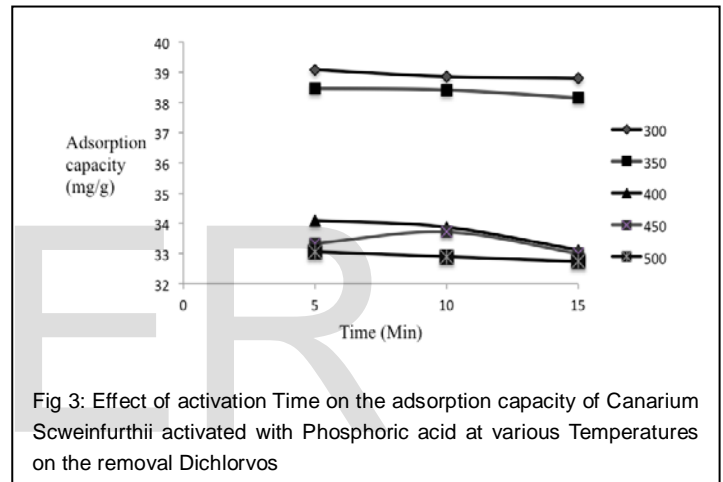


Fig 3: Effect of activation Time on the adsorption capacity of *Canarium Schweinfurthii* activated with Phosphoric acid at various Temperatures on the removal Dichlorvos

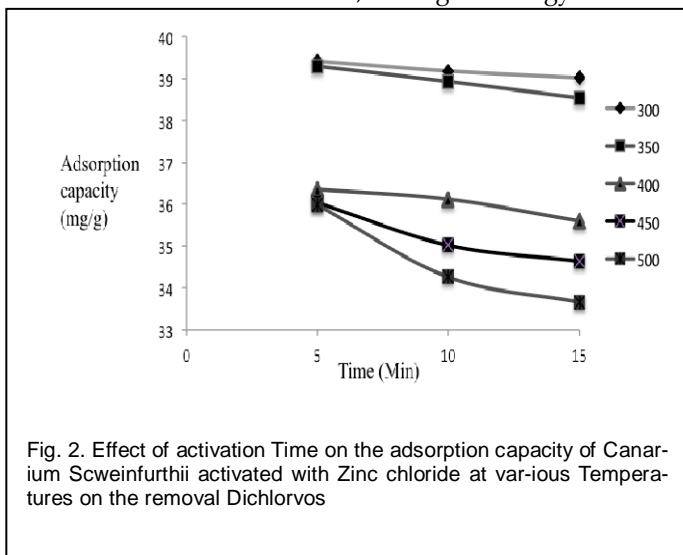


Fig. 2. Effect of activation Time on the adsorption capacity of *Canarium Schweinfurthii* activated with Zinc chloride at various Temperatures on the removal Dichlorvos

rated and adsorption begins at low energy site which result in a decreases in adsorption efficiencies [13]. The low removal efficiency of the activated carbon with increase in activation time can be explained in term of insufficiency of micropore structure formation with increased time of activation.

4 CONCLUSION

In conclusion, the chemical activation process was used to prepare activated carbon with *Canarium schweinfurthii* seed shell as agricultural waste with Zinc Chloride and Phosphoric acid. Under the experimental conditions investigated, the resulting activated carbons are efficient in the removal of Dichlorvos, 39.42 mg/g are removed at activation temperature of 300°C and activation time of 5 minutes with zinc chloride as the activating agent. From the results obtained 39.08 mg/g is removed at activation temperature of 300°C and activation time of 5 minutes using Phosphoric acid as activating agent. The result obtained signifies the optimal conditions for producing high adsorption capacity activated carbon. It was found that Dichlorvos as a pollutant of environment could be removed from aqueous solution using granular activated carbon from *Canarium schweinfurthii* seed shell.

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