

# Adsorption of Carbofuran on Granulated Activated Carbon from *Canarium Schweinfurthii* Seed Shell

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**Abstract**— Series of activated carbon have been prepared from *Canarium Schweinfurthii* Seed Shell (CSSS) with Zinc Chloride ( $ZnCl_2$ ) and Phosphoric acid ( $H_3PO_4$ ) as chemical activation agent. The activated carbon samples were prepared by carbonization at 300 °C, 350 °C, 400 °C, 450 °C and 500 °C for 5, 10, 15, 20 and 25 minutes with the chemical agents. The quality of the samples has been evaluated in terms of carbofuran adsorption. The optimum conditions for activated carbon production were evaluated based on the determination of the adsorption capacity of carbofuran. The maximum unit capacity for carbofuran adsorption was 719.6 mg/g at activation temperature of 500°C and activation time of 20 minutes with zinc chloride as the activating agent. Using Phosphoric acid as activating agent it was found that the optimum unit capacity for carbofuran was 675.6mg/g at activation temperature of 450°C and activation time of 20 minutes. This study showed that activated carbons produced with the activating agent can be utilized as effective matrices for Carbofuran removal from aqueous medium.

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

## 1 INTRODUCTION

Activated carbon is a very effective adsorbents for a wide range of toxic, organic, vapour phase species encountered in domestic and industrial situations [1]. It is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area, thus, producing reasonably cheap and excellent adsorbent [2], [3]. Activated carbon is widely used as adsorbents on either liquid or gas phase processed due its highway porous texture and large adsorption capacity [4]. The source of the most commonly used activated carbon in commercial practice is peat, coal, lignite, and wood materials like coconut husks, nutshells, corn cobs, timber saw dusts etc [5], [6], [7], [8]. On the other hand agricultural wastes are lignocellulosic wastes that offer an inexpensive additional source of activated carbon. [8]. Usually, the surface properties of the produced activated carbon are affected by the starting material and activation condition. Activated carbons are produced by three methods, physical, chemical and combined (physical and chemical) procedures [9]. Physical activation involves carbonization followed by gasification at higher temperatures, but in chemical activation the source material is impregnated with chemical reagent such as  $ZnCl_2$  or  $H_3PO_4$  then heated at moderated temperatures [8].

In the past decade there has been considerable research

concerning the preparation of low cost activated carbon from agricultural wastes such as coconut husk, rice husks, grass, corn cobs etc [6], [7], [8], [9]. Carbofuran is a broad-spectrum carbamate insecticide, acaricide, and nematicide. It is applied in granular form or aerially. It may be used on a variety of crops, the most common including strawberries, alfalfa, corn, grapes, soybeans, and wheat. Carbofuran is used to control soil-dwelling and foliar-feeding insects such as corn root-worm, wireworms, boll weevils, mosquitoes, alfalfa weevil, aphids, and white grubs [11]. It has very low ability to be adsorbed, thus it can be easily leached into groundwater.

In general, Carbofuran can be degraded by the chemical hydrolysis and biological degradation process. The Carbofuran degradation can take place more rapidly in alkaline condition. A report showed that only 1% of insecticide sprayed would go to insect pest and 99% would be a residue in the environment [12]. Carbofuran may be effectively removed from drinking water by activated carbon adsorption [13]. There are only a few papers on Carbofuran residue analysis [14]. Because of the extensive and long-term use of pesticides in agriculture, public concerns have arisen over possible contamination of food, water, and air. In addition, the adverse effects on human health have begun to receive much attention. Therefore, careful monitoring of the presence of these Carbofuran in water is one avenue to avoid possible exposure.

CSSS is very cheap and available in the middle belt region of Nigeria; studies on the utilization of CSSS as a precursor for manufacturing activated carbons are minimal or none. In addition information concerning the adsorption of Carbofuran onto CSSS has not been reported. Therefore, the aim of this study is to describe the feasibility of the preparation of activated carbons from agricultural waste CSSS by chemical activation with  $ZnCl_2$  and  $H_3PO_4$  and to present a study on the adsorption of Carbofuran using effective and simple analytical methods to detect the presence of Carbofuran. The adsorption

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capacity of the activated carbon produced on Carbofuran were analyzed and used to establish the appropriate operating conditions including activation temperature and time.

## 2 MATERIAL AND METHODS

### 2.1 Preparation of Samples

In the present study, CSSS has been used for the preparation of activated carbon. The seed shells were washed, sundried and crushed using 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 samples were chemically activated by the addition of 1M ZnCl<sub>2</sub> and 1M H<sub>3</sub>PO<sub>4</sub> separately. The sample was activated in the furnace for 5, 10, 15, 20 and 25 minutes at 300, 350, 400, 450 and 500°C. The activated carbon produced was washed with distilled water to remove the excess of the activating agents. They were oven dried at 120°C and stored in sealed air tight polythene bags for further experiments. All the chemicals used were of analytical reagent grade obtained from BDH and E.Merck except where stated otherwise. Carbofuran stock solution (50 mg/L) was prepared in distilled water using Carbofuran granules. The working solutions were obtained by diluting the stock solution in distilled water.

### 2.2 Batch Mode Adsorption Studies

Batch mode adsorption studies were carried out with 50mg of the activated carbons and 10ml of the stock solution (50mg/L), agitated at 200rpm in a mechanical shaker at room temperature (25°C). Different granular activated carbon produced were allowed to equilibrate with constant initial concentration of Carbofuran solution (C<sub>0</sub>=50ppm). 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 Carbofuran was estimated spectrophotometrically at 465nm using p-aminoacetophenone [15].

The amount of Carbofuran adsorbed per mass unit of granular activated carbon in equilibrium condition, Q<sub>e</sub>, was calculated using the equation below

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

Where V is the Volume of Carbofuran solution, C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium concentrations, respectively, of the Carbofuran solutions in mg/L and M is the mass of the granular activated carbon in g the equation gives Q<sub>e</sub> in mg of Carbofuran adsorbed per g of granular activated carbon.

### 2.3 Spectrophotometric Determination of Carbofuran

A solution of p-aminoacetophenone (1%, w/v) was prepared in HCl (1:4). An aqueous solution (0.2%, w/v) of sodium nitrite was prepared. 4M NaOH was prepared in distilled water. 0.2% Sodium nitrite (3ml) was added dropwise to 50ml of diazotized p-aminoacetophenone with string. The diazo-

tized compound was kept in the cold ice bath at 0°C-5°C.

0.5ml of 5% NaOH was added to the solution of the Carbofuran and was allowed to stand for 10min for complete hydrolysis. 1.5ml of diazotized p-aminoacetophenone was added and allowed to stand for 5min with occasional shaking to ensure complete coupling. 1ml of NaOH was added. Absorbance of red brown polymethine dye was measured at 465nm.

## 3 RESULTS AND DISCUSSIONS

### 3.1 Effect of activation time

Activation time is one of the most important factors affecting the adsorption capacity of activated carbon. The results in Figures 1 and 2 have shown that the adsorption capacities of the activated carbon increases with activation time up to 8 minutes where the maximum adsorption capacity is obtained. With the increase in activation time, the random arrays of pore structures had more appeared due to the progress of activation reaction between the activating agents and the carbon and the release of volatile matter. With increasing activation time, probably due to the violent attack of carbon by chemical materials, the opening of pores is clearly damaged and partly burnt, resulting in the widening of pore diameters i.e. increasing of mesopore volume and decreasing of micropore volumes [17]. H<sub>3</sub>PO<sub>4</sub> acts in two ways during the chemical activation of lignocellulosic feedstuff: (i) promoting the rupture of bonds in the biopolymer constituents and (ii) forming cross-links through cyclization and condensation processes [18]. This observation revealed that an increase in activation time from 15 to 25 minutes caused some of the pores to become larger or even collapse, thus contributed to the reduction in surface area [18].

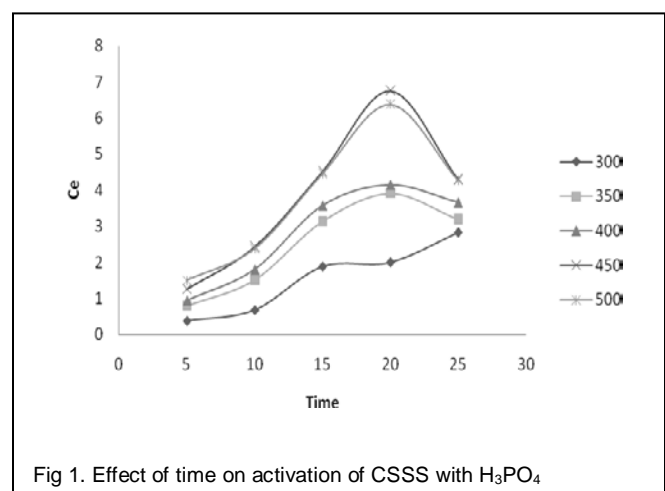


Fig 1. Effect of time on activation of CSSS with H<sub>3</sub>PO<sub>4</sub>

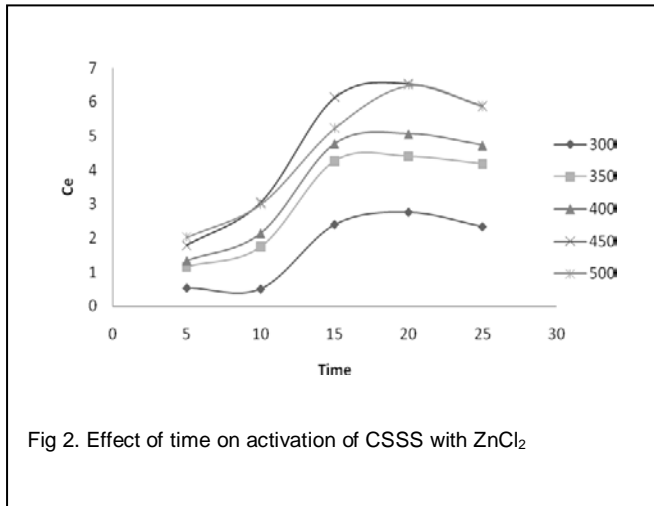


Fig 2. Effect of time on activation of CSSS with ZnCl<sub>2</sub>

### 3.2 Effect of Activation Temperature

Activation temperature imposed greater effect on activated carbon yield and carbofuran adsorption. The activation temperature is an important parameter in shaping the pure structure of activated carbon. At higher activation temperature, the removal of volatile matter becomes extensive resulting in lower solid yield [19], [20]. The results show that the adsorption capacities increases significantly with an increase in temperature of activation. After activation with Zinc Chloride at 500°C, the surface area of the sample is doubled compared with the adsorption capacities at 300°C, thus creating a larger internal surface area and a maximum porous structure. The difference in the optimum activation temperature has been accredited to reactivity of the chemical structure in lignocellulosic materials [18] [21]. As the temperature increased, the C-ZnCl<sub>2</sub> reaction rate was increased, leading to a decrease in carbon yield [18].

However, the adsorption capacities of samples activated with Phosphoric acid at 500°C are relatively lower and the activated carbon was able to remove 521.8 mg/g of the adsorbate. Since only pores larger than the size of adsorbate molecule were accessible to the adsorbent, it is believed that some pores in the activated samples were blocked by decomposition products of the organic constituents, thus inhibiting the accessibility of the active sites for the adsorption in the of sample activated with phosphoric acid. Nady et al. [18] have reported that H<sub>3</sub>PO<sub>4</sub> combines with organic species forming phosphates and polyphosphate bridges that connect biopolymer fragments, thereby partially hindering the contraction in materials when temperature increases. These bridges become unstable above 450°C. Thus their loss produces a contraction in the material which will result in a decrease in porosity [18]. After activation with Zinc chloride at same temperature the adsorption capacities increase. The effectiveness of Zinc Chloride as activation agent has been widely noted in literature [22]. The salt might have penetrated into the CSSS and effectively removed the decomposition products during activation at higher temperature. The activation process of ZnCl<sub>2</sub> was effective in creating well developed pores, resulting to large surface areas activated carbons with good microporous struc-

ture [18]. Generally the result shows that at low temperatures activation was adsorption was lower due to inefficient heat transfer.

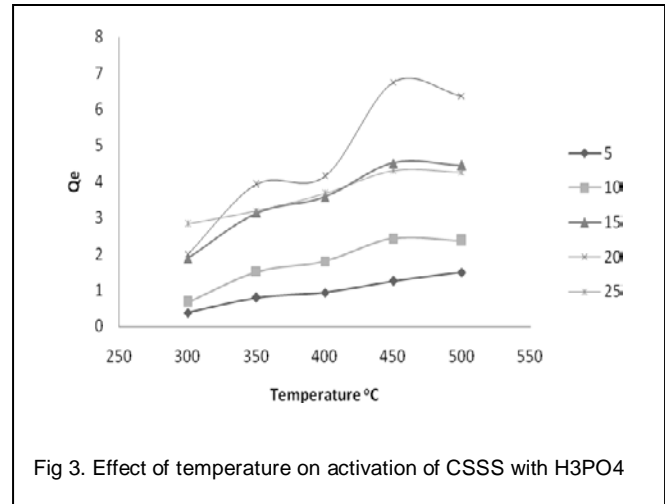


Fig 3. Effect of temperature on activation of CSSS with H<sub>3</sub>PO<sub>4</sub>

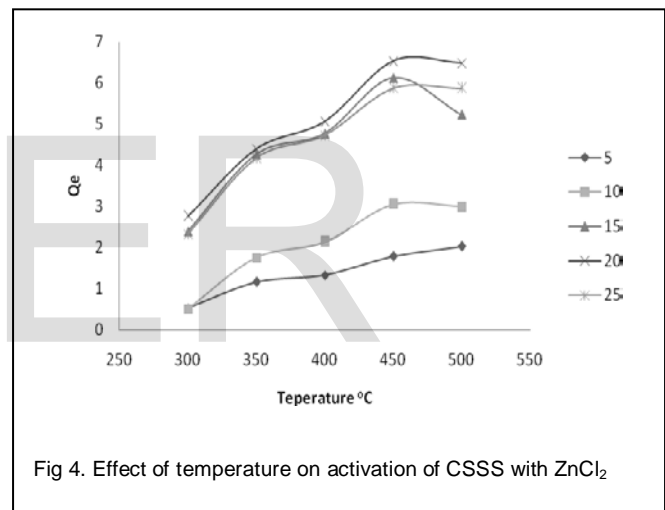


Fig 4. Effect of temperature on activation of CSSS with ZnCl<sub>2</sub>

## 4 CONCLUSION

Chemical activation process was used to prepare activated carbons from agricultural waste, CSSS, with Zinc Chloride and Phosphoric acid in the present study. The results have confirmed that varying time and temperature of activation produces a significant influence on the textural and adsorptive properties of the activated carbon produced. Under the experimental conditions investigated, the resulting activated carbons are efficient in the removal of Carbofuran. From the results, activating at a temperature of 500°C, for 20 minutes using Zinc Chloride as activating agent produced the highest adsorption capacity CSSS activated carbon. It has been found that Carbofuran as a pollutant of environment could be removed from aqueous solution using granular activated carbon from CSSS. This preliminary and adsorption studies show that the activated carbon prepared from CSSS can be used effectively in the treatment of pesticides from wastewaters. As the raw material is an agricultural waste, its application in the

treatment process is expected to be commercially viable.

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