

# Adsorptive Removal of Synthetic Organic Compounds in Aqueous Solutions by Fresh Nipa Palm Fronds

Pereware Adowei

Department of Pure and Industrial Chemistry, University of Port Harcourt, Port Harcourt, Nigeria

## Email address:

pereware.adowei@uniport.edu.ng

## To cite this article:

Pereware Adowei. (2024). Adsorptive Removal of Synthetic Organic Compounds in Aqueous Solutions by Fresh Nipa Palm Fronds. *Science Frontiers*, 5(1), 13-23. <https://doi.org/10.11648/sf.20240501.13>

**Received:** January 3, 2024; **Accepted:** January 15, 2024; **Published:** February 1, 2024

**Abstract:** Adsorptive removal of contaminants in wastewater is distinctive because the technique is simple, effective and with low cost, however, the flexibility of the adsorption process is actually contingent on the sorption abilities of the adsorbent. Nipa palm has been tested in several studies to be effective due to its porous structure and surface properties. Hence, the objective of this paper was to evaluate the adsorptive removal of synthetic organic compounds (SOCs) in aqueous solutions using carbonized and surface-modified carbons produced from Nipa Palm (*Nypa Fruticans* Wurmb) fronds using chemical oxygen demand (COD) as the index of measurement. Data obtained for the present investigation revealed that percent COD reduction of SOC by the carbons ranged between 93.81 – 96.67%, while COD reduction capacity estimated by Langmuir-type model was between 1.77 - 11.83 mg/g at ambient temperature and at an optimum pH of 8.5. Thermodynamic assessment by Gibbs free energy ( $\Delta G^\circ$ , KJ/mol) revealed that  $\Delta G^\circ$  values were negative (from - 1.45 KJ/mol to - 5.89 KJ/mol). The results obtained show that Nipa palm could be a beneficial source for the development of an eco-friendly and locally available activated carbon for removal of organic contaminants from domestic and industrial wastewaters.

**Keywords:** Synthetic Organic Compounds, Chemical Oxygen Demand, Adsorption, Nipa Palm, Carbonized Carbon, Wastewater

## 1. Introduction

Synthetic organic compounds (SOCs) have been identified in wastewater and water supplies and could be removed by adsorption techniques [1-3]. These compounds have adverse health effects. Also, their presence in water may reduce dissolved oxygen concentrations, which is detrimental to aquatic life [4-5]. Therefore, treatment of wastewater is necessary to correct its characteristics in such away that its use or final disposal can take place without causing an adverse impact on the ecosystem of the recipient water bodies. Conventional treatment methods for removal of synthetic organic Chemicals from aqueous solution, such as photochemical degradation, biological degradation, coagulation, chemical oxidation and adsorption have been investigated by several workers [6-10].

However, the adsorption is the most successful of these methods due to its simplicity and low cost [11-12]. Chemical oxygen demand (COD) in water analysis is critical in wastewater for determining the amount of organic waste

contamination in the water. Waste that is high in organic matter requires treatment to reduce the amount of organic waste before discharging into recipient waters. Chemical Oxygen Demand (COD) is a major parameter used as routine surrogate tests for measuring the load of organic carbon into the environment [13]. Also, COD is a cheap method for the determination of organic load in waste water [14]. The objective of this paper, therefore, is to investigate the feasibility of removing selected synthetic organic compounds (SOCs) in aqueous solutions using physically (distil H<sub>2</sub>O) carbonized, acidic (3.27 M, H<sub>3</sub>PO<sub>4</sub>) activated and basic (10% KOH solution) activated carbons produced from fresh Nipa Palm (*Nypa Fruticans* Wurmb) Fronds using chemical oxygen demand (COD) as the index of measurement.

## 2. Materials and Methods

*Nipa Palm Sample Collection:* Fresh fronds of the samples were collected during low tide at the Ogbunabali waterfront along Eastern-Bypass in Port Harcourt, Nigeria.

**Processing of Nipa Palm Sample:** Fresh fronds of Nipa palm (*Nypa fruticans* Wurmb) collected during low tide at the Ogbunabali waterfront along Eastern Bypass in Port Harcourt, Nigeria were carefully separated into the fronds and the stalks. Both fronds and stalks were washed with plenty of water to remove surface impurities and sun dried. This was followed by oven drying at 110°C for several days [15]. The dried leaves were grounded using a grinder (Landa Cisa 2D) to obtain the fine powdered biomass, which was sieved to mesh size 106  $\mu\text{m}$  to obtain the dried leaves biomass, which was used to produce the carbonized and surface-modified carbons. The 106  $\mu\text{m}$  mesh Tyler sieve used in this research work was obtained from the Geology laboratory of the University of Port Harcourt.

**Chemicals:** The ferrous ammonium sulphate, ferroin indicator, iron sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), hydrogen peroxide  $\text{H}_2\text{O}_2$  (30% W/V),  $\text{H}_2\text{SO}_4$ , sodium hydroxide NaOH, acetic acid ( $\text{CH}_3\text{COOH}$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), mercuric sulphate  $\text{HgSO}_4$ , silver sulphate  $\text{Ag}_2\text{SO}_4$ , manganese oxide, 10% HCl, potassium hydroxide 10% KOH (0.9 M), 10% (3.27 M)  $\text{H}_3\text{PO}_4$ , 2-(N,N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) (ii) kerosene and (iii) n-propanol and commercial activated carbon (AquaNucha).

**Carbonization of Biomass:** The dried Nipa palm biomass from the fronds were carbonized by taking about  $25 \pm 0.01$  g of the Nipa palm leaves biomass (< 110 mesh size) was introduced into a clean and pre-weighed crucible containing 25 ml of distilled water in a 1:1 ratio to form a paste. The paste was transferred to a clean and pre-weighed crucible and placed in a muffle furnace (Carbolite Sheffield England, LMF4) and was heated gradually to 550°C for 10 min. The mixture was allowed to remain at this temperature in the oven for 2 hrs, after which it was poured from the crucible into a bowl containing some ice block crystals. The excess water was drained and the samples were sun dried [16, 2]. The carbonized sample was washed, using 10% HCl to remove surface ash, followed by hot water wash and rinsing with distilled water to remove residual acid [17]. The solids were then sun dried, followed by oven drying at 100°C for one hour [18] and then weighed. The dried sample was sieved through a 106- $\mu\text{m}$  mesh Tyler sieve and the fractions < 106  $\mu\text{m}$  were collected for use. This is the carbonization step which produced the *physically carbonized carbon (PCC)*. The sealed oven provided an oxygen-deficient condition under which the biomass was thermally decomposed to porous carbonaceous materials and hydrocarbon compounds.

**Activation of Biomass:** The activated carbons were prepared by a one-step pyrolysis method [19, 20]. The activated carbons produced were called (i) Acidic reagent activated carbon (AAC) and (ii) Basic reagent activated carbon (BAC).

**Acidic Reagent Activated Carbon (AAC):**  $25 \pm 0.001$  g Nipa palm leaves biomass was placed in a beaker containing 25 ml of 10% (3.27 M)  $\text{H}_3\text{PO}_4$  solution. The content of the beaker was thoroughly mixed and heated to form a paste. The paste was transferred to a clean and pre-weighed crucible and

placed in a furnace and was heated gradually to 500°C for 10 min. After activation, the mixture was allowed to cool to room temperature and weighed. The pyrolyzed carbons were washed, using 10% HCl to remove surface ash, followed by rinsing with distilled water to remove residual acid [16, 2] until a neutral pH was achieved. The sample was then dried in an oven at 110°C overnight. The final product was ground and sieved through a 106  $\mu\text{m}$  mesh Tyler sieve. Fractions < 106  $\mu\text{m}$  were collected and kept in an air-tight container for use. Washing was complete when a pH of  $7 \pm 0.5$  was ascertained [21, 2].

**Basic Reagent Activated Carbon (BAC):**  $25 \pm 0.001$  g Nipa palm leaves biomass was placed in a beaker containing 25 ml of 10% KOH solution. The 0.9 M standard solution was made by adding 49.93 grams of KOH into 1000ml distilled water. The content of the beaker was thoroughly mixed and heated to form a paste. The paste was transferred to a clean and pre-weighed crucible and placed in a furnace and was heated at 500°C for 10 min. After activation, the mixture was allowed to cool to room temperature and weighed. The pyrolyzed carbons were washed, using 10% HCl to remove surface ash, followed by rinsing with distilled water to remove residual acid [16, 2] until a neutral pH was achieved. The sample was then dried in an oven at 110°C overnight. The final product was ground and sieved through a 106  $\mu\text{m}$  mesh Tyler sieve. Fractions < 150- $\mu\text{m}$  were collected and kept in an air-tight container for use. Washing was complete when a pH of  $7 \pm 0.5$  was ascertained [21, 2].

**Commercial Activated Carbon (CAC):** The commercial activated carbon used in this research has the trade name AquaNuchar SA-1500. AquaNuchar is a premium wood based activated carbon for treatment and purification of potable water. AquaNuchar was used as the control.

**Preparation of Synthetic Organic Chemicals used in this work:** Three synthetic organic chemicals (SOCs) were used in this research work. They are (i) 2-(N,N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) (ii) kerosene and (iii) n-propanol.

(i) **Preparation of Standard Solutions:** A 1.0 g of water-soluble Na-salt of DMABA crystals were weighed on a top loading electronic balance and dissolved in 300 ml distilled water. The mixture was diluted and made up to 1000 ml giving a stock solution with concentration of 1000 mg/l. Working DMABA solutions with concentrations (mg/l) of 20, 40, 60, 80, and 100 were prepared from the stock solution. The COD of the working solutions were measured as the initial COD ( $\text{COD}_i$ ) and the COD of the distilled water was determined to give the blank COD.

(ii) **Preparation of Standard Kerosene Solutions:** (ii) **Preparation of Standard Kerosene Solutions:** The following mixtures (in ml) of kerosene: isopropanol ratios were made. 10:90, 20:80, 30:70, 40:60, and 50:50 made in five different 100 ml volumetric flasks. The mixtures were thoroughly shaken by shaker. The COD of the mixtures were measured as the initial COD ( $\text{COD}_i$ ). The COD of the 90, 80, 70, 60 and 50 ml isopropanol were also measured and considered to give the blank COD.

Also, a mass weight can be used to prepared the standards of kerosene by using the average density of kerosene ( $0.81 \text{ mg/cm}^3$ ), the mass equivalent in each volume was calculated as in equation 1.

$$\text{Density, g/ml} = \frac{\text{mass (g)}}{\text{volume (ml)}} \quad (1)$$

10 ml of isopropanol was added to each beaker as a solvent for kerosene. The mixture was diluted to 100 ml with isopropanol giving working kerosene solutions with concentrations (mg/l) of 16.20, 32.40, 48.60, 64.80, and 81.00. The COD of the working solutions were measured as the initial COD ( $\text{COD}_i$ ) and the COD of the isopropanol was determined to give the blank COD.

(iii) *Preparation of Standard n-Propanol Solutions*: 20, 40, 60, 80, and 100 ml of n-propanol were measured into five different beakers. Using the density of n-propanol ( $0.803 \text{ mg/cm}^3$ ), the mass equivalent in each volume was calculated as was done for kerosene. 10 ml of distilled water was added to each beaker. The mixture was diluted to 100 ml with distilled water giving working n-propanol solutions with concentrations (mg/l) of 16.06, 32.12, 48.18, 64.24, and 80.30. The COD of the working solutions were measured as the initial COD ( $\text{COD}_i$ ) and the COD of the distilled water was determined to give the blank COD.

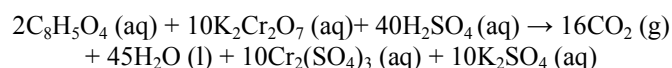
### 2.1. Determination of Effect of Initial Concentration at Constant Temperature

2.0 g of PCC, AAC, BAC of  $106 \mu\text{m}$  mesh particle size and CAC were separately placed in a series of 150 ml plastic sample containers containing 50 ml working solution of DMABA, kerosene and n-propanol with the following concentrations (mg/l): 20, 40, 60, 80, and 100. The suspensions were shaken at room temperature ( $30 \pm 2^\circ\text{C}$ ) using agitation speed (150 rpm) with a contact time of 60 min. At the end of 60 min, the suspensions were allowed to stand on the bench for 30 min to separate and then filtered using Whatman No 40 filter paper. The clear supernatant SOC solutions were analyzed for final COD ( $\text{COD}_f$ ).

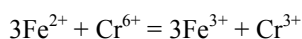
### 2.2. Determination of Chemical Oxygen Demand (COD)

COD measurement is a two-step process [22, 2] – Digestion and Determination. The chemistry of these two processes is explained below.

**Digestion Step**: organic matter is oxidized by dichromate ions in sulphuric acid to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . During heating the dichromate ions ( $\text{Cr}_2\text{O}_7^{2-}$ ) form orange-colored solutions.



**Determination Step**: During titration FAS reacts with dichromate solution to form green coloured chromic ion solution. After end point, FAS reacts with indicator to form brown colour solution



To determine the COD of each sample, 10 ml 0.125 M standard potassium dichromate solution was added to 20 ml of the different solutions and the clear solutions in a 250 ml round-bottom flask. 1.0 g silver sulphate and 40 ml conc. sulphuric acid were added in small portions with careful swirling until the silver sulphate was completely dissolved. A few glass beads were added to serve as anti-bumping aid, and the flask was connected to reflux condenser. The mixture was heated gently for 10 minutes or more as the case may be, after which the content of the flask was cooled. 50 ml distilled water was flushed through the condenser, and the cooling was completed under running tap water. 2 drops of indicator solution were added and the resulting mixture titrated with standardized 0.025 M ferrous ammonium sulphate (FAS) solution until there was a change in colour from yellow-green via blue-green to reddish brown. 20 ml distilled water as blank and 20 ml clear solution from batch adsorption studies were also taken through the same process and their COD values determined.

**Calculation of COD from Experimentation**: The COD values of the respective solutions and blank were estimated [2] as presented in eqn (2).

$$\text{COD as mg O}_2/\text{L} = \frac{(A-B) \times m \times 8000}{V_s} \quad (2)$$

Where A = ml of ferrous ammonium sulphate (FAS) used for blank; B = ml of FAS used for sample; M = molarity of FAS;  $V_s$  = Volume of sample used (ml) and 8000 = milliequivalent weight of oxygen  $\times 1000 \text{ ml/L}$ .

**Calculation of % COD Reduction**: Calculation of percent reduction of chemical oxygen demand (COD) in the solutions after being contacted with the carbons was estimated [2] by Eqn (3).

$$\% \text{ COD Removed} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \times 100 \quad (3)$$

Where  $\text{COD}_i$  = COD concentration of initial SOC working solutions before interactions with the carbons (mg/L) and  $\text{COD}_f$  = COD concentration of SOC working solutions after interactions with the carbons (mg/L).

### 2.3. Calculation of COD Reduction Capacity at Equilibrium

The apparent capacity of the carbons for COD reduction were examined [2] at using the relationship expressed in eqn (4)

$$q_e = \frac{(\text{COD}_i - \text{COD}_f)V}{w} \quad (4)$$

Where  $q_e$  = COD reduction capacity (mg/g) of SOC removed at equilibrium,  $\text{COD}_i$  = COD concentration of SOC solution before interaction with the carbons (mg  $\text{O}_2/\text{L}$ ).  $\text{COD}_f$  = COD concentration of SOC solution after interaction with the carbons (mg  $\text{O}_2/\text{L}$ ). V = volume of SOC solution used (L) and w = weight of carbon (g).

## 2.4. Calculation of Equilibrium Model Parameters

The batch experimental data were subjected to two popular adsorption equilibrium models - the Langmuir and Freundlich adsorption models.

The *Langmuir isotherm* was employed in this study for the estimation of maximum adsorption capacity as expressed [23] in eqn (5).

$$q_e = \frac{q_{max}K_L C_e}{1 + K_L C_e} \quad (5)$$

Where  $K_L$  is Langmuir constant ( $Lmg^{-1}$ ) and  $q_{max}$  is the maximum reduction of COD upon complete saturation of the carbon surface ( $mg/l$ )  $C_e$  is the equilibrium COD reduction and  $q_e$  is adsorption capacity.

The linearized form of the above equation after rearrangement is given [23] by equation 6.

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \left(\frac{C_e}{q_{max}}\right) \quad (6)$$

Rearranged into the form of  $y = mx + c$

$$\frac{C_e}{q_e} = \frac{K_L}{q_{max}} + \left(\frac{1}{q_{max}}\right) C_e \quad (7)$$

A plot of  $C_e / q_e$  versus  $C_e$  give a straight-line graph with a slope of  $1/q_{max}$  and an interception of  $K_L / q_{max}$  on the y axis.

The Freundlich model was used to estimate the extent of adsorption. The linear equation [23] is given as equation (8)

$$\log q_e = \log K_L + \frac{1}{n} \log C_e \quad (8)$$

To determine the constants  $K_L$  and  $n$ , a plot of  $\log q_e$  versus  $\log C_e$  should be linear and the slope and intercept yield the empirical constants.

## 2.5. Calculation of Adsorption Favourability

The favourability of the adsorption system was predicted using the separation factor as presented ( $S_F$ ) [24] in eqn (9).

$$S_F = \frac{1}{1 + K_L C_0} \quad (9)$$

Where  $S_F$  is a dimensionless factor,  $C_0$  is the initial SOC's concentration and  $K_L$  is the Langmuir constant.

## 2.6. Calculation of Thermodynamic Parameters

The apparent Gibbs free energy was obtained [25] using equation (10)

$$\Delta G^0 = -RT \ln K_L \quad (10)$$

Where  $K_L$  is the thermodynamic equilibrium constant of the Langmuir model.

## 2.7. Analytical Precision and Quality Control

Care was taken during sample collection and preservation. Glassware was properly cleaned and reagents were of analytical grade. Reagent blanks, method blanks and working

standards/solutions were prepared freshly. For quality control purpose a commercial activated carbon (CAC) with the trade name *Aqua Nucha* was purchased and used as a control. *Aqua Nucha* was supplied by Rovet Scientific Ltd, Benin City.

## 2.8. Statistical Analysis of Experimental Data

The reliability of experimental results was obtained by carrying out triplicate analysis and calculation of the mean, standard deviations, standard errors and analysis of variance (ANOVA).

## 3. Results and Discussion

The microstructure of the Nipa palm biomass and carbonized carbon were studied by scanning electron microscopy (SEM); energy dispersive x-ray (EDX) and FTIR which has been published previously [2].

*COD Reduction of SOC's Solutions:* The chemical oxygen demand (COD) concentrations play an important role in the use and re-use of wastewater. COD reduction from solutions of known concentrations ( $mg/L$ ) of DMABA, kerosene and n-propanol was investigated using PCC, AAC, BAC and CAC under optimum conditions. The process conditions used were 12.3 grams of carbon, 17.62 cm bed height, ambient temperature, pH = 6.5 and flow rate 15 ml/min. The COD concentration decreased significantly in the treated SOC solution as compared to the raw SOC solution (Table 1).

**Table 1.** Percent COD reduction of raw SOC's solutions (in  $mg/L$ ).

Carbons	Raw SOC solution	Treated SOC solution	% COD reduction
DMABA			
PCC	44.73	9.16	95.67
AAC	44.73	19.65	96.23
BAC	44.73	6.47	96.85
CAC	44.73	1.11	97.51
Kerosene			
PCC	67.42	13.121	95.37
AAC	67.42	22.609	96.13
BAC	67.42	10.241	96.67
CAC	67.42	1.843	97.26
n-propanol			
PCC	22.44	1.387	93.81
AAC	22.44	1.198	94.66
BAC	22.44	1.054	95.30
CAC	22.44	1.054	95.303

The results showed that the physically activated carbons (PCC), acid activated carbon (AAC), base activated carbon (BAC) and commercial activated carbon (CAC) were effective for removal of COD from the SOC's contaminated water samples. For raw DMABA sample, the reduction in COD was from  $44.73 \text{ mgL}^{-1}$  to  $1.96 \text{ mgL}^{-1}$  (PCC),  $1.65 \text{ mgL}^{-1}$  (AAC),  $1.47 \text{ mgL}^{-1}$  (BAC),  $1.11 \text{ mgL}^{-1}$  (CAC), with a removal efficiency of 95.67 (PCC), 96.23% (AAC), 96.85% (BAC), and 97.51% (CAC). For raw kerosene sample, the initial COD obtained was  $67.42 \text{ mg L}^{-1}$ . The reduction in COD was from  $67.42 \text{ mgL}^{-1}$  to  $3.12 \text{ mgL}^{-1}$  for PCC with 95.37% removal efficiency,  $67.42 \text{ mg L}^{-1}$  to  $2.61 \text{ mg L}^{-1}$  for AAC with a removal efficiency of 96.13%,

67.42 mg L<sup>-1</sup> to 2.24 mgL<sup>-1</sup> for BAC with 96.67% removal efficiency and 67.42 mgL<sup>-1</sup> to 1.84 mgL<sup>-1</sup> for CAC amounting to 97.26% removal efficiency. The initial COD of the raw water sample containing some volume of n-propanol was found to be 22.44 mgL<sup>-1</sup>. This sample was treated with PCC, AAC, BAC and CAC respectively and the COD measure thereafter. The results show that, the reduction in COD was from 22.44 mgL<sup>-1</sup> to 1.05 mgL<sup>-1</sup> (PCC), 1.39 mgL<sup>-1</sup> (AAC), 1.20 mgL<sup>-1</sup> (BAC), 1.05 mgL<sup>-1</sup> (CAC), with removal efficiencies of 95.30% (PCC), 93.81% (AAC), 94.66% (BAC), and 95.30% (CAC). The study results agree with those of Horsfall and Co-worker [26] who studied the performance of a stratified sand filter in removal of chemical oxygen demand, total suspended solids and ammonia nitrogen from high-strength wastewater. They also stated that the system hydraulic loading rate of 10 L/m<sup>2</sup>/d gave a filter COD, TSS and total TKN loading rate of 14, 3.7 and 2.1 g/m<sup>2</sup>/d, respectively and produced consistent COD and TSS removals of greater than 99% and an effluent NO<sub>3</sub>-N concentration of 42 mg L<sup>-1</sup> (accounting for an 86% reduction in total nitrogen (Tot-N)).

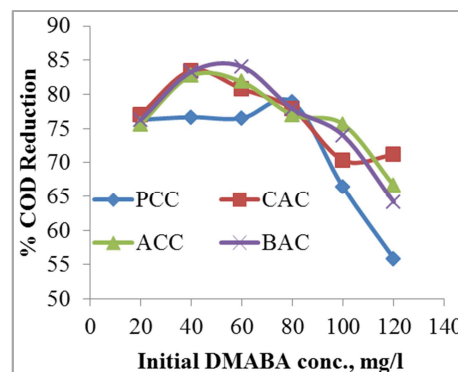
The maximum percentage reduction of COD under optimum operating conditions was 95.67% (PCC), 96.23% (AAC), 96.85% (BAC) for DMABA, 96.13% (PCC), 96.13% (AAC), 96.67% (BAC) for kerosene and 95.30% (PCC), 93.81% (AAC), 94.66% (BAC) for n-propanol respectively and with CAC this reduction was 97.51% (DMABA), 97.26% (kerosene) and 95.30% (n-propanol) respectively. Since the adsorption capacity of the Nipa palm leaves carbons are comparable with that of CAC for reduction of COD, it could be a beneficial technique for treatment of domestic wastewater generated in dispersed areas. Therefore, COD adsorption capacity of CAC of the SOC's could be used as a control parameter for COD measurement of organic contaminants.

### 3.1. Effect of Initial SOC Concentration on COD Reduction

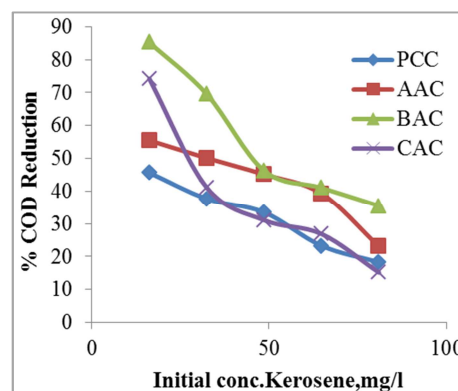
The relationship between the percent COD reduction of 2-(N,N-Dimethyl-4-aminophenyl) azo-benzene carboxylic acid (DMABA) and their respective chemical oxygen demand (COD) for PCC, AAC, BAC and CAC are presented in Figure 1. The optimal COD reduction in DMABA by PCC, AAC, BAC and CAC were 82.7%, 76.7%, 83.5%, and 83.3% respectively at initial concentration of 80 mg/l. The data showed that COD reduction increased from lower concentration of 20 mg/l to give maximum reduction around 40 mg/l and reduced. It is evident from the data that the percent COD reduction which measures the adsorption efficiency of the carbons decreased with the increase in initial DMABA concentration in the solution. As can be seen from the figure 2, the COD reduction by PCC, AAC, BAC and CAC decreased with increasing kerosene concentration.

The data showed that maximum COD reduction of over 80% was achieved for BAC at lower concentration, while PCC and AAC recorded 45.6 and 55.5% respectively. CAC was able to reduce COD from the initial concentration by 74.2%. The data showed that BAC is a better adsorbent for COD reduction of kerosene contaminated effluent at lower concentrations. The influence of the initial concentration of n-propanol in the solutions on the degree of COD reduction

on PCC, AAC and BAC from Nipa palm leaves biomass and commercial activated carbon (CAC) was studied.

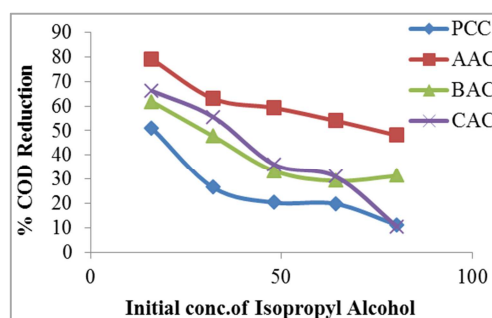


**Figure 1.** Effect of initial concentration of DMABA solution on COD reduction by PCC, AAC, BAC and CAC at 30°C.



**Figure 2.** Effect of initial concentration of kerosene solution on COD reduction by PCC, AAC, BAC and CAC at 30°C.

The experiments were carried out at fixed adsorbent dose (400 mg/100 ml) in the test solution, 29 ± 1°C room temperature, pH (6.7) and at different initial concentrations of DMABA (50, 100, 150, 200 and 250 mg/L) for 60 mins. The effect of initial n-propanol concentration on COD reduction is shown in figure 3. The adsorption yield showed a decreasing trend as the initial n-propanol concentration was increased. At lower concentrations, all n-propanol present in the adsorption medium could interact with the binding sites on the surface of the adsorbents so higher adsorption yields were obtained. At higher concentrations, lower adsorption yields were observed because of the saturation of the adsorption sites.



**Figure 3.** Effect of initial concentration of n-propanol solution on COD reduction by PCC, AAC, BAC and CAC at 30°C.



### 3.2. Equilibrium Adsorption Models for Batch Experimental Data

Equilibrium adsorption models are fundamental criteria in the design of adsorption systems because they provide physicochemical data for evaluating the applicability of the adsorption processes as a unit operation. They also provide noticeable information on the adsorbent – adsorbate system. To facilitate the estimation of the sorption capacities, experimental data from the various experiments from this research work were fitted to the Langmuir and Freundlich equilibrium adsorption models.

### 3.3. Langmuir Adsorption Isotherm

Langmuir isotherm has a theoretical basis and assumed that a surface consists of a given number of equivalent sites where a species can physically or chemically stick. In order to facilitate the estimation of the adsorption capacity at various initial SOC concentrations, the Langmuir adsorption isotherm, which is a typical model for monolayer adsorption was applied to the experimental data. The Langmuir equation assumes that there is no interaction between adsorbate molecules and that once an adsorbate molecule occupies a site; no further sorption can take place at that site. Theoretically, therefore a saturation value is reached beyond which no further sorption can take place. Therefore, the Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the carbon surface. The

plot of specific sorption ( $\frac{C_e}{q_e}$ ) against equilibrium

concentration ( $C_e$ ) for DMABA, kerosene and n-propanol on PCC, AAC, BAC and the CAC are shown in figures 4, 5, 6 respectively. The Langmuir equilibrium isotherm model for the sorption of DMABA onto PCC, AAC, BAC and CAC are presented in figure 4. The Langmuir maximum COD reduction ( $q_{max}$ ) capacity (mg/g) in aqueous solutions of synthetic organic chemicals (SOCs) upon complete surface saturation of the carbons are 21.50 mg/g (DMABA), 6.20 mg/g (kerosene), 13.84 mg/g (n-propanol) for PCC, 8.73 mg/g (DMABA), 3.18 mg/g (kerosene), 19.67 mg/g (n-propanol) for AAC, 57.83 mg/g (DMABA), 7.17 mg/g (kerosene), 25.75 mg/g (n-propanol) for BAC and 62.60 mg/g (DMABA), 21.70 mg/g (kerosene), 27.80 mg/g (n-propanol) for CAC respectively.

The adsorption capacity,  $q_{max}$ , which is a measure of the maximum adsorption capacity corresponding to complete monolayer surface coverage, showed that BAC has a higher mass capacity for DMABA (57.83 mg/g) and n-propanol (25.75 mg/g) than kerosene (7.17 mg/g). The adsorption coefficients ( $K_L$ ,  $dm^3/g$ ), which is related to the apparent energy of adsorption for synthetic organic chemicals (SOCs) investigated are presented in table 1. The adsorption coefficient was greater for kerosene ( $9.49 \times 10^{-1} dm^3/g$ ) in AAC than for n-propanol ( $2.88 \times 10^{-1} dm^3/g$ ) and DMABA ( $5.63 \times 10^{-1} dm^3/g$ ). This could mean that the energy of adsorption is not very favourable for AAC for kerosene. Comparing the adsorption coefficients

values of the carbons from Nipa palm and that of the CAC shows that, BAC is the best carbon obtained from the Nipa palm biomass.

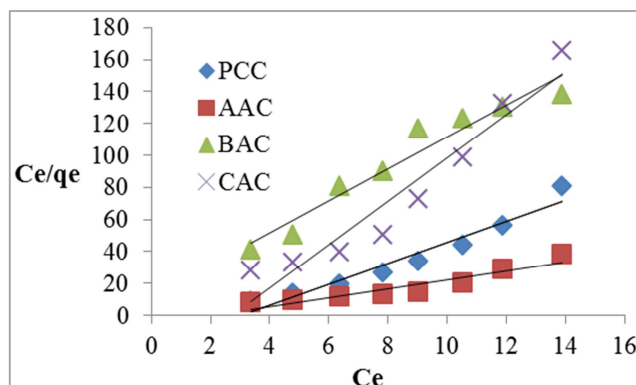


Figure 4. Langmuir equilibrium isotherm model of COD reduction of DMABA solution by PCC, AAC BAC and CAC.

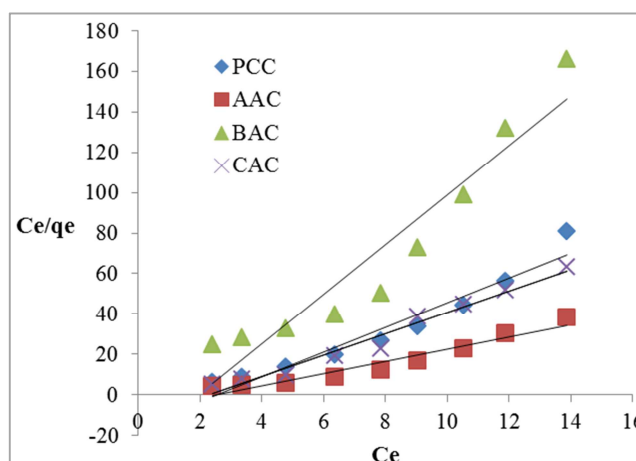


Figure 5. Langmuir equilibrium isotherm model of COD reduction of kerosene solution by PCC, AAC BAC and CAC.

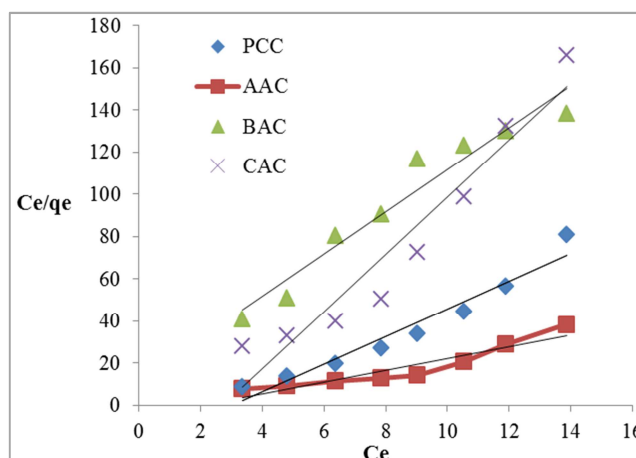


Figure 6. Langmuir equilibrium isotherm model of COD reduction of n-propanol solution by PCC, AAC BAC and CAC.

The linear isotherm parameters of  $q_{max}$ ,  $K_L$ , and the coefficient of determinations are presented in Tables 2, 3 and 4 respectively.

**Table 2.** Langmuir maximum COD reduction ( $q_{max}$ ) capacity (mg/g) for synthetic organic chemicals (SOCs) in aqueous solutions during the COD reduction by the carbons.

	PCC	AAC	BAC	CAC
	$mg\ g^{-1}$			
DMABA	6.50	8.73	11.83	16.60
Kerosene	1.20	1.18	1.77	2.70
n-Propanol	3.84	1.67	5.75	7.80

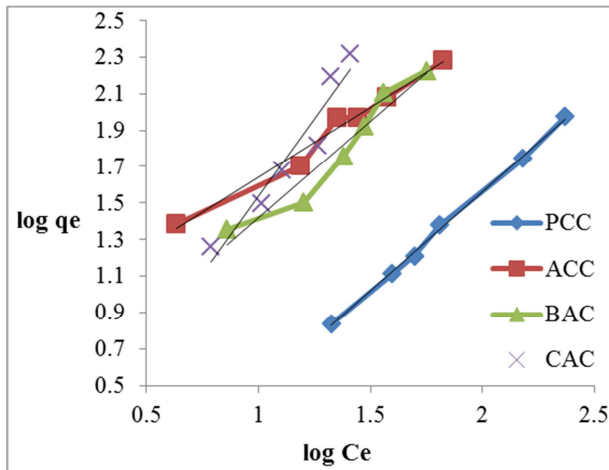
**Table 3.** Langmuir constants ( $K_L$ ,  $dm^3/g$ ) for synthetic organic chemicals (SOCs) in aqueous solutions during the COD reduction by the carbons.

	PCC	AAC	BAC	CAC
DMABA	$8.70 \times 10^{-1}$	$9.49 \times 10^{-1}$	$7.0 \times 10^{-1}$	$2.0 \times 10^{-1}$
Kerosene	$1.02 \times 10^{-1}$	$2.88 \times 10^{-1}$	$3.28 \times 10^{-1}$	$1.17 \times 10^{-1}$
n-Propanol	$2.02 \times 10^{-1}$	$5.63 \times 10^{-1}$	$1.03 \times 10^{-1}$	

### 3.4. Freundlich Adsorption Isotherm

Freundlich adsorption isotherm model is an empirical equation and can be used for non-ideal sorption that involves heterogeneous adsorption. The model is used to approximate data for physical adsorption systems especially liquids. The Freundlich isotherm was used to estimate the adsorption intensity of COD reduction by fitting the experimental data.

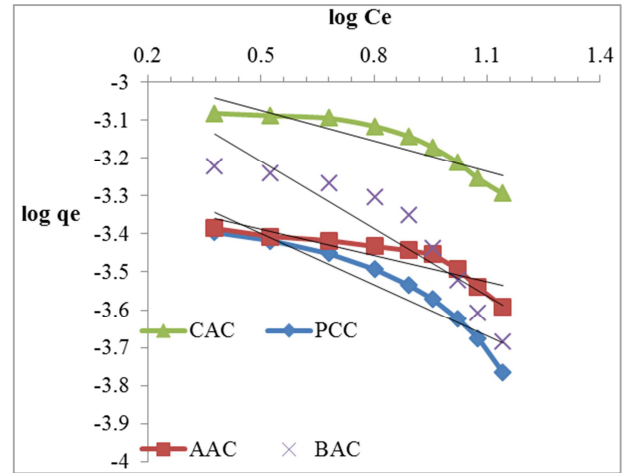
The linear Freundlich isotherms for the COD reduction representing the sorption of SOC's onto the carbons (PCC, AAC, BAC and CAC) are presented in figures 7, 8 and 9 for DMABA, kerosene and n-propanol respectively. The Freundlich constant  $K_F$  is the equilibrium partition coefficient related to the bonding energy. It can be defined as the adsorption or distribution coefficient and be related to the degree or extent of adsorption. In practice, large  $K_F$  values enhance adsorption.



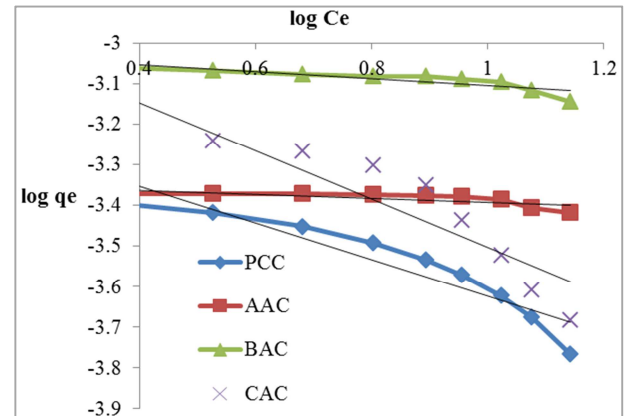
**Figure 7.** Freundlich equilibrium isotherm model of COD reduction of DMABA solution by PCC, AAC, BAC and CAC.

The  $K_F$  values for DMABA, kerosene and n-propanol on the different carbons are 0.207 (DMABA), 0.502 (kerosene), 0.502 (n-propanol) for PCC, 0.570 (DMABA), 0.515 (kerosene), 0.524 (n-propanol) for AAC, 0.447 (DMABA), 0.464 (kerosene), 0.480 (n-propanol) for BAC and 0.783 (DMABA), 0.468 (kerosene), 0.464 (n-propanol) for CAC respectively.

The Freundlich isotherm model parameter  $1/n$  is a measure of the adsorption intensity. It was chosen to estimate the COD reduction intensity of SOC's by the carbons investigated. If  $n = 1$ , the separation of SOC's between the two phases (aqueous system and adsorbate) is independent of concentration. In this case  $K_F = K$  and the isotherm is linear. A favourable COD reduction measured corresponds to a value of  $1 < n < 10$ .



**Figure 8.** Freundlich equilibrium isotherm model of COD reduction of kerosene solution by PCC, AAC, BAC and CAC.



**Figure 9.** Freundlich equilibrium isotherm model of COD reduction of n-propanol solution by PCC, AAC, BAC and CAC.

The value of  $n$  indicates the affinity of the SOC's towards the carbon and it provides a rough estimate of the strength or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. The intensity of COD reduction for DMABA was found to be 0.357, 0.1605, 0.6209 and 0.8765 for PCC, AAC, BAC and CAC respectively, while for kerosene the reduction intensity for the three Nipa palm carbons and the commercial carbons are 0.315 (PCC), 0.306 (AAC), 0.343 (BAC), 0.340 (CAC). The COD reduction intensity for n-propanol is 0.433, 0.428, 0.799 and 0.851 for PCC, AAC, BAC and CAC. The reduction intensity is higher for DMABA than n-propanol and kerosene indicating preferential sorption for DMABA in a mixture of the three SOC's. Among the three carbons produced from nipa palm

leaf biomass, BAC had a higher intensity for the three SOC than the other two carbons (AAC and PCC). The behavior of BAC is comparable to the CAC.

Examination of the Freundlich plots and their corresponding isotherm parameters reveals that the Freundlich isotherm is also an appropriate model to describe the COD reduction behavior by the three carbons and the commercial carbon. The regression coefficients of determination,  $r^2$ , from the linearization of the two isotherm

models are listed in Table 4. Based on the  $r^2$  values, the Langmuir isotherm provides an excellent model to describe the COD reduction behaviour of the three SOC by the Nipa palm derived carbons. While the Freundlich isotherm produce a reasonable fit to the experimental data for DMABA than kerosene and n-propanol. The  $r^2$  values for DMABA are greater than kerosene and n-propanol in both Langmuir and Freundlich isotherms for PCC, AAC and BAC.

Table 4. Linear isotherm coefficients of determination ( $r^2$ ).

Carbons	$r^2$ values for Langmuir model				$r^2$ values for Freundlich model			
	PCC	AAC	BAC	CAC	PCC	AAC	BAC	CAC
DMABA	0.945	0.875	0.981	0.994	0.899	0.898	0.906	0.927
Kerosene	0.938	0.932	0.986	0.988	0.879	0.779	0.824	0.814
n-propanol	0.945	0.875	0.995	0.998	0.879	0.560	0.727	0.824

### 3.5. Prediction of Adsorption Favourability

In 1978, Poots and co-workers [27] proposed a separation index ( $S_i$ ) to predict whether a sorption process is favourable or unfavourable in a batch adsorption process using the Langmuir isotherm adsorption coefficient ( $K_L$ ). The dimensionless parameter,  $S_i$ , indicates that, if  $S_i > 1$ , there is an unfavourable interaction between adsorbate, and therefore adsorption may not be possible; if  $S_i = 1$ , there is a linear relationship between adsorbate and adsorbent interaction and the possible interaction is a mixture of physisorption and chemisorptions mechanism. When  $0 < S_i < 1$ , there is a favourable interaction between adsorbate and adsorbent, and the predominant mechanism is physisorption. If  $S_i = 0$ , there is an indefinite sticking between adsorbate and adsorbent, and the predominant mechanism is chemisorptions.  $S_i$  was predicted using the Langmuir isotherm constant and the COD reductions obtained from the initial concentrations of SOC. The relationship between the dimensionless separation index ( $S_i$ ) and the initial concentrations of DMABA, kerosene and n-propanol were plotted and presented in figures 10, 11 and 12.

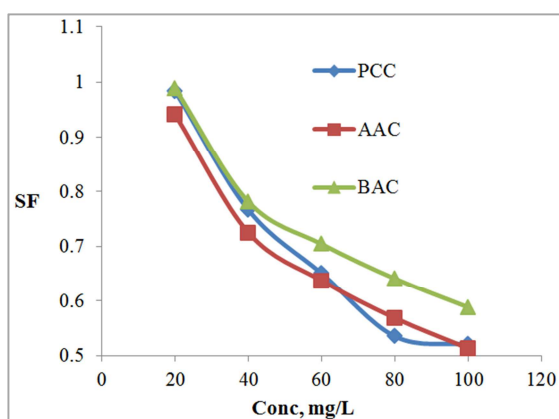


Figure 10. Separation factor profile as a function of initial DMABA concentration.

$S_i$  values for DMABA on the PCC, AAC and BAC ranged from 0.54 – 0.92, 0.54 – 0.97 and 0.61 – 0.98 respectively. The

separation index for kerosene on the carbons are 0.19 – 0.35, 0.32 – 0.65 and 0.35 – 0.68 for PCC, AAC and BAC respectively, while n-propanol has separation index of 0.22 – 0.56 (AAC), 0.38 – 0.75 (PCC) and 0.55 – 0.85 (BAC) respectively.

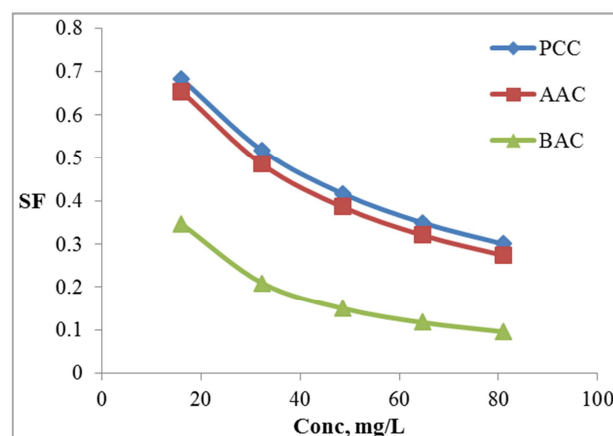


Figure 11. Separation factor profile as a function of initial Kerosene concentration.

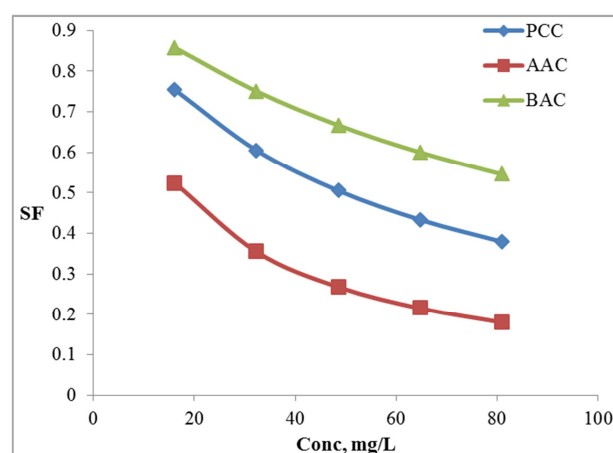


Figure 12. Separation factor profile as a function of initial n-propanol concentration.

The results for the separation indices indicate that, the interaction between the carbons derived from Nipa palm



leaves biomass (PCC, AAC and BAC) and the various synthetic organic chemicals (DMABA, kerosene and n-propanol) investigated are favourable and the predominant mechanism is physisorption since all the values of  $S_i < 1$ .

### 3.6. Thermodynamic Treatment of Batch Experimental Data

According to thermodynamic laws, in an isolated system, where energy cannot be gained or lost, the entropy is the driving force. However, in environmental chemistry, both enthalpy and entropy must be considered in order to determine whether a process will occur spontaneously. [28]. Consequently, the SOC reduction equilibrium constant,  $K_L$ , obtained from the Langmuir isotherm model was used to compute the apparent Gibbs free energy  $\Delta G^\circ$  of sorption, which is a fundamental criterion of spontaneity. Adsorption process is said to be spontaneously at a given temperature if  $\Delta G^\circ$  is a negative quantity. Values of  $\Delta G^\circ$  up to  $-20$  kJ/mol are consistent with electrostatic interactions between sorption sites and adsorbate corresponding to physisorption, while  $\Delta G^\circ$  values more negative than  $-40$  kJ/mol involve charge sharing or transfer of electrons between adsorbent and adsorbate to form a coordinate bond. The apparent Gibbs free energy ( $\Delta G^\circ$ , kJ/mol) of COD reduction in the three SOC solutions by Nipa palm derived and commercial carbons as computed are presented in Table 5. The values of  $\Delta G^\circ$  computed for DMABA on PCC, AAC, BAC and CAC are  $-3.51$  kJ/mol,  $-0.13$  kJ/mol,  $-5.899$  kJ/mol and  $-4.056$  kJ/mol respectively. The apparent Gibbs free energy for kerosene on the carbons were  $-5.753$  kJ/mol (PCC),  $-3.137$  kJ/mol (AAC),  $-2.809$  kJ/mol (BAC) and  $-5.408$  kJ/mol (CAC) at  $30^\circ\text{C}$ , while that of n-propanol was  $-4.031$  kJ/mol (PCC),  $-1.447$  kJ/mol (AAC),  $-5.729$  kJ/mol (BAC) and  $-3.03$  kJ/mol (CAC) at  $30^\circ\text{C}$ . The negative values of  $\Delta G^\circ$  indicate that the COD reduction process and the interaction of the three SOC solutions with the Nipa palm derived and commercial carbon are all spontaneous in nature requiring minimal amount of energy. The process may occur at ambient temperature without the aid of external energy. When a chemical reaction has a negative  $\Delta G^\circ$ , the reaction is said to be exothermic because  $\Delta G^\circ$  is the change in energy of a system and the change in its entropy. If the effect of a reaction is to reduce  $G$ , the process will be spontaneous so  $\Delta G^\circ$  is negative.

Since the values of  $\Delta G^\circ$  obtained are  $< -20$  kJ/mol, it means that the interactions between SOC solutions and the carbons

are electrostatic, which involve no charge sharing or electron transfer between adsorbent and adsorbate. The apparently low values of  $\Delta G^\circ$  indicate that the dominant mechanism between the SOC solutions and the carbons is physisorption.

**Table 5.** Computation of apparent Gibbs free energy ( $\Delta G^\circ$ , kJ/mol) of COD reduction in the three SOC solutions by Nipa palm derived and commercial carbons.

Carbons	PCC $G^\circ$ , kJ/mol	AAC	BAC	CAC
DMABA	-3.51	-1.31	-5.899	-4.056
Kerosene	-5.753	-3.137	-2.809	-5.408
n-propanol	-4.031	-1.447	-5.729	-3.03

Analytical results are incomplete without an estimation of their reliability. Reliability is a statistical measure of the overall consistency of the analytical process. Therefore, the measure of uncertainties associated with the computed results in this work was obtained by subjecting the numerical data of the COD reduction capacity studies to one-way ANOVA statistical treatment using the F-ratio test. The internal structures of the COD reduction capacity data estimated from the Langmuir isotherm model were used to estimate the one-way analysis of variance (ANOVA) at  $\alpha = 0.05$  by considering the carbons as the objects and the SOC as the variable using the null hypothesis ( $H_{01}$ ) that compared the potential capacities of the three Nipa palm carbons (PCC, AAC and BAC) to remove SOC in aqueous solution. The null hypothesis states that the capacity of the three carbons is all equal at the 0.05 significant level and then one-way ANOVA was computed. The result shows that,  $F_{exp}(0.74) < F_{crit}(4.07)$  meaning that there is no difference in the potential capacities of the three Nipa palm carbons (PCC, AAC and BAC) to remove SOC in aqueous solution at the 0.05 significant level. A significance level of 0.05 indicates a 5% risk of concluding that a difference exists when there is no actual difference. To determine whether any of the differences between the means are statistically significant, the p-value obtained from the computation (Table 6) is compared with the significance level (0.05) used to assess the null hypothesis. Because the p-value is 0.5582, which is greater than the significance level of 0.05, ( $P > 0.05$ ) the null hypothesis is accepted and the conclusion is that there is no significant differences between the COD reduction capacity of PCC, AAC and BAC. This means that COD reduction capacity of SOC in aqueous solution by PCC, AAC and BAC are all equal and that the three carbons produced from Nipa palm are all potential adsorbents for removing SOC in aqueous solution.

**Table 6.** One-Way Analysis of Variance (ANOVA) at  $\alpha = 0.05$  to compare the Nipa palm carbons and CAC.

Source of Variation	SS	df	MS	F	P-value	F crit
Carbons	55.3681	3	18.456	0.73837	0.55817	4.06618
Within Groups	199.964	8	24.9955			
Total	255.332	11				

SS = sums of square; df = degrees of freedom; MS = means of square; P-value = Probability value; F = calculated F ratio value; F-crit = critical F-ratio value

## 4. Conclusions

The data revealed that the COD reduction is dependent on

the concentration of the SOC solutions present in solution. The thermodynamic assessment of the experimental data using the Gibbs free energy ( $\Delta G^\circ$ , kJ/mol) reveals that  $\Delta G^\circ$  values were relatively small and also negative for the interaction

between the three SOC's and Nipa palm derived carbons. The Gibbs free energy  $\Delta G^\circ$  of adsorption is used to measure spontaneity of a reaction. Adsorption process is said to be spontaneously at a given temperature if  $\Delta G^\circ$  is a negative quantity. Values of  $\Delta G^\circ$  up to  $-20$  kJ/mol indicates electrostatic interactions between sorption sites and adsorbate and this corresponds to physisorption, while  $\Delta G^\circ$  values more negative than  $-40$  kJ/mol involve charge sharing or transfer of electrons between adsorbent and adsorbate to form a coordinate bond. The Gibbs free energy ( $\Delta G^\circ$ , kJ/mol) of COD reduction of the three SOC's solutions by Nipa palm derived and commercial carbons shows that, all the  $\Delta G^\circ$  values are negative. This indicates that the COD reduction process between the three SOC's with the Nipa palm derived and commercial carbons are all spontaneous in nature requiring minimal amount of energy. Again, all the values of  $\Delta G^\circ$  obtained are less than  $-20$  kJ/mol. This means that the interactions between SOC's and the carbons are electrostatic, which involve no charge sharing or electron transfer between SOC's and the carbons. These apparently low values of  $\Delta G^\circ$  indicate that the dominant mechanism between the SOC's and the carbons is physisorption.

In conclusion, the series of batch adsorption experiments conducted in this work reveal that Nipa palm derived carbons are capable of reducing organic contaminants in aqueous solutions. Production of carbons from the leaves of Nipa palm is feasible, economical and environment friendly. These removal potentials are significantly comparable to the commercial activated used to validate the carbons. The feasibility was further assessed by using separation factor; and the data obtained revealed that the interaction between the Nipa palm derived carbons and the various SOC's investigated are favourable and the predominant mechanism is physisorption. The outcome of this investigation has revealed that carbons developed from Nipa palm leaves are an attractive option for organic contaminants removal from aqueous solution.

## Abbreviations

AAC: Acidic Reagent Activated Carbon

BAC: Basic Reagent Activated Carbon

PCC: Physically Carbonized Carbon

CAC: Commercial Activated Carbon

COD: Chemical Oxygen Demand

DMABA: 2-(N, N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid

SOC: Synthetic Organic Compounds

## Acknowledgments

The authors wish to acknowledge the kind support through a Grant with No W5574-1 provided to author by the International Foundation for Science (IFS), Sweden.

## ORCID

0009-0009-8973-5591

## Conflicts of Interest

The author declares no conflicts of interest.

## References

- [1] Adowei, P. Spiff, A. I. & Abia, A. A. (2014). Evaluation of Carbonized and Surface-Modified Carbon Produced from Nipa Palm (*Nypa fruticans Wurmb*) Leaves for the Removal of 2-(N,N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) in Aqueous Solution *Acta Chim. Pharm. Indica: 4*(3), 2014, 146-156.
- [2] Adowei, P; Abia, A. A; & Spiff, A. I (2015). Physicochemical Characteristics of Biocarbons obtained from Nipa Palm (*Nypa fruticans Wurmb*) Leaves. *Research. Journal of Chemical Sciences*. Volume 5 No. 1, pp 18-26.
- [3] Adowei, P; Wariboko, E & Markmanuel, D, (2020). Removal of Low concentration of. Kerosene from water using Nipa palm (*Nypa fruticans Wurmb*) fruit fibre. *International Journal of Research Volume 8 No. 6* pp 1-9.
- [4] Adowei, P; & Abia A. A (2016). Chemical Oxygen Demand (COD) Attenuation of Methyl Red in Water using Biocarbons obtained from Nipa palm (*Nypa fruticans Wurmb*) Leaves. *Journal of Applied Sciences & Environmental Management*. Volume 20 No. 4 pp 1163-1176.
- [5] Abia, A. A., Horsfall, M. Jnr & Didi, O (2003). The Use of Chemically Modified and Unmodified Cassava Waste for the Removal of Cd, Cu and Zn ions from Aqueous Solution. *Bioresource Techno.* 90 345–348.
- [6] Verla, A. W; Adowei, Pereware; & Verla, E. N. (2014). Physicochemical and Microbiological Characteristic of Palm Oil Mill Effluent (POME) in Nguru - Aboh Mbaise, Eastern Nigeria *Acta Chimica. Pharmaceutica. Indica: 4*(3), 2014, 119-125.
- [7] Horsfall, M. Jnr & Abia, A. A (2003). Sorption of Cd (II) and Zn (II) ions from Aqueous solutions by Cassava Waste Biomass (*Manihot esculenta* Cranz). *Wat. Res.* 37: 4913–4923.
- [8] Epkete, O. A; Spiff, A. I; Horsfall, M. Jnr; & Adowei, Pereware. (2012). Adsorption of Phenol and Chlorophenol in aqueous solution on a commercial activated carbon in batch sorption systems. *Innovations in Science and Engineering*. 2(2) 72-78.
- [9] Horsfall, M. Jnr.; Spiff, A. I. & Abia, A. A. (2004). Studies on the Influence of Mercaptoacetic Acid (MAA) Modification of Cassava (*Manihot esculenta* Cranz) Waste Biomass on the Adsorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  from Aqueous Solution. *Bull. Korean Chem. Soc.* Vol. 25(7), 969–976.
- [10] Horsfall, M. Jnr & Spiff, A. I. (2005) a. Effect of metal ion concentration on the biosorption of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$  by *Caladium bicolor* (wild cocoyam). *African J. of Biotech.* Vol. 4(2) pp 191-196.
- [11] Abechi, S. E, Gimba, C E, Uzairu, A, & Dallatu, Y A (2013). Preparation and Characterization of activated carbon from Palm Kernel Shell by Chemical Activation. *Research Journal of Chemical Sciences*. 3(7) 54-61.
- [12] Adinata, D, Wan Daud WMA, Aroua MK. (2007) Preparation and characterization of activated carbon from palm shell by chemical activation with  $\text{K}_2\text{CO}_3$ . *Bioresource Technology* 98: 145-49.

- [13] Fadini, Pedro Sérgio; Jardim, Wilson F.; Guimarães, & José Roberto (2004). Evaluation of Organic Load Measurement Techniques in a Sewage and Waste Stabilisation Pond. *J. Braz. Chem. Soc.*, 15(1): 131-135.
- [14] Ademiluyi, F T; & Braide, O (2012). Effectiveness of Nigerian Bamboo Activated with Different Activating Agents on the Adsorption of BTX. *Journal of Appl. Sci. Environ. Manage.* 16(3) 267–273.
- [15] Adowei, P; Abia, A. A; & Okorosaye-Orubite, K (2017). Study of kerosene elimination in water by steam-modified and acid-modified carbons made from nipa palm (*Nypa fruticans* Wurmb) leaves. *Journal, Chemical Society of Nigeria. Volume 42, No. 1 pp 75-8.*
- [16] Gimba C, Ocholi O, & Nok A. (2004). Preparation of A. C from Agricultural wastes II. Cyanide binding with activated carbon matrix from groundnut shell. *Nigerian journal of scientific research. Bioresour. Technol.* 97, 401-406.
- [17] Fan, M., Marshall, W., Daugaard, D., & Brown, R. C., (2003), Steam activation of chars produced from oat hulls and cornstover, *Bioresource Technol.*, 93, 103–117.
- [18] Itodo A. U., Abdulrahman F. W., Hassan L. G, Maigandi S. A., & Itodo H. U. (2010). Physicochemical parameters of Adsorbents from locally sorted  $H_3PO_4$  and  $ZnCl_2$  modified Agricultural wastes (Groundnut shells, Shea nut shells, Poultry wastes and Poultry droppings). *New York Science Journal* 3(5) 17–24.
- [19] Ash B, Satapathy D, Mukherjee PS, Nanda B, Gumaste JL, & Mishra BK, (2006). Characterization and application of activated carbon prepared from coir pith. *J. Sci. Ind. Res.* 65 1008-1012.
- [20] Sugumaran, P, Priya. S. V, Ravichandran, P. & Seshadri, S (2012). Production and Characterization of Activated Carbon from Banana Empty Fruit Bunch and *Delonix regia* Fruit Pod. *Journal of Sustainable Energy & Environment* 3: 125-132.
- [21] Ahmedna M, Marshal W, & Rao M. (2000). Production of Granular activated carbon from selected Agriculture by products. *Bioresource and Technology.* 71(2): 113–123.
- [22] Wayne Boyles (1997). The Science of Chemical Oxygen Demand (COD). Technical Information Series, Booklet No. 9. Pp8-9.
- [23] Horsfall, M. Jnr., Abia, A. A.; & Spiff, A. I. (2006). Kinetic studies of Adsorption of  $Cd^{2+}$ ,  $Cu^{2+}$ , and  $Zn^{2+}$  ions from Aqueous solutions by cassava (*Manihot sculenta* Cranz) tuber bark waste. *Bio Resource Tech.* 97, pp 283–291.
- [24] Ekpete, O. A. & Horsfall, M. Jnr (2011). Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste (*Telfairia occidentalis* Hook F). *Research Journal of Chemical Sciences.* Vol. 1(3) June 2011 10-17.
- [25] Wankasi, D., Horsfall, M. Jnr; & Spiff, A. I., (2005). Desorption of  $Pb^{2+}$  and  $Cu^{2+}$  from Nipa palm (*Nypa fruticans* Wurmb) biomass. *Afr. J. Biotechnol.* 4, 923-927.
- [26] Horsfall, M. Jnr; & Spiff, A. I. (2005) b. Effect of Temperature on the Sorption of  $Pb^{2+}$  and  $Cu^{2+}$  from Aqueous Solution by *Caladium bicolor* (Wild Cocoyam) Biomass. *Electronic Jour. Of Biotech.* Vol. 8(2); pp 162-169.
- [27] Poots, V. J. P., G. Mackay & J. J. Healy, (1978). Removal of basic dye from effluent using wood as an adsorbent. *J. Water Pollut. Control Federation*, 50: 926-935.
- [28] Tarawou, T; Wankasi, D; & Horsfall, M (2010). Sorption kinetic study on the removal of basic blue-9 dye using activated carbon produced from water spinach. *Int. J. Biol. Chem. Sci.* 4. (3). 703–709.