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Fixed-Bed Column Adsorption Studies of Synthetic Organic Chemicals Using Carbonized and Surface-Modified Carbons from Nipa Palm Leaves

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Abstract: Batch adsorption isotherm data do not always provide accurate scale-up facts for real systems. Consequently, it is necessary to carry out fixed-bed column adsorption studies, which provide essential design parameters that are necessary for column scale-up. Hence, the objective of this paper was to evaluate the fixed-bed column adsorption studies to remove synthetic organic chemicals (SOC) using carbonized and surface-modified carbons from nipa palm leaves. Carbonized and surface-modified carbons were produced by single-step pyrolysis after soaking the Nipa palm (*Nypa fruticans* Wurmb) leaves biomass with H_2O, H_3PO_4 and KOH respectively while using chemical oxygen demand (COD) as the index of measurement. The SOCs solutions of concentration 100 mg/L at pH 6.5 were fed into the column from the top in a reservoir at the downward gravity flow rate of 15 mL/min and the effluent collected at the bottom at 30 minutes interval for 4 hours, quantity of the prepared adsorbent was packed in the column to yield the desired bed height of 7.62 cm containing 12.3 g of carbon. The optimum performance (mg cm^{-3}) of the carbons are 10.16 (PCC), 9.024 (AAC) and 12.442 (BAC) for DMABA; 12.95 (PCC), 10.51 (AAC) and 16.64 (BAC) for kerosene and 9.568 (PCC), 6.651 (AAC) and 13.903 (BAC) for n-propanol) respectively. The breakthrough curve was analyzed using the Adams–Bohart, Thomas, and bed depth service time (BDST) mathematical models. The behaviors of the breakthrough curves were defined by the Thomas model at different conditions. The BDST model showed good agreement with the experimental data, and the high values of correlation coefficients ($R^2 \geq 0.9646$) obtained indicate the validity of the bed depth service time model for the present column system.

Keywords: Synthetic Organic Chemicals, Adsorption, Fixed-Bed, Nipa Palm, Chemical Oxygen Demand

1. Introduction

Synthetic organic chemicals (SOCs) are organic compounds that originate from domestic, commercial and industrial activities. Many of these compounds have been identified in wastewater and water supplies [7-11]. These compounds have adverse health effects. Also their presence in water column may reduce dissolved oxygen concentrations, which is detrimental to aquatic life [6, 2]. Therefore, treatment of wastewater is necessary to correct its characteristics in such a way that its use or final disposal can take place without causing an adverse impact on the ecosystem of the receiving 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 [18, 27-29, 43]. However, Adsorption is the most successful of these methods due to its simplicity and low cost [1, 4]. Chemical oxygen demand (COD) water analysis is critical in wastewater for determining the amount of organic waste contamination in the water. Waste that's 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 parameters used as routine surrogate tests for measuring the load of organic carbon into the environment [20]. Also, COD is a cheap method for the determination of organic load in waste water [3]. Batch adsorption are useful for small volumes of effluents in a laboratory scale process, however, it would not

be very useful in scale-up process when large industrial wastewater effluents are involved. Fixed-bed adsorption of pollutants involves percolation of wastewater through a percolating material [34]. The design and theory of fixed-bed adsorption systems focuses on establishing the shape of the breakthrough curve and its velocity through the bed [5]. Breakthrough and bed volumes are employed in the determination of the performance of a fixed-bed described using the concept of breakthrough curve [42, 17]. In this study, column studies were conducted to evaluate the adsorption capacity of carbons from Nipa palm fresh leaves for SOCs removal. Successful design of a column adsorption process requires prediction of the concentration–time profile or breakthrough curve for the effluent. Prediction of the outlet concentration usually involves solution of a set of non-linear partial differential equations governing the flow and mass transfer by sophisticated numerical scheme with proper identifications of many system parameters. However, in a fixed bed, the adsorbate is continuously in contact with a given quantity of fresh adsorbent thus providing the required concentration gradient between adsorbent and adsorbate for adsorption. The design and theory of fixed bed adsorption systems centers on establishing the shape of the breakthrough curve and its velocity through the bed. Various mathematical models are available to describe fixed-bed adsorption. Among these are the Adam-Bohart and Thomas Kinetic models [25-27, 30, 37] which were employed in this work.

The objective of this paper, therefore, was to carry out fixed bed column adsorption studies to remove synthetic organic chemicals (SOC) using carbonized and surface-modified carbons from nipa palm leaves. The carbonized and surface-modified carbons were produced by single-step pyrolysis after soaking the Nipa palm (*Nypa fruticans* Wurmb) leaves biomass with H_2O, H_3PO_4 and KOH respectively while 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 separated from the fronds and the stalks and leaves carefully removed. Both fronds, leaves 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. The dried leaves were grounded using a grinder (Landa Cisa 2D) to obtain the fine powdered biomass, which was sieved to mesh size 106 μm to obtain the dried leaves biomass, which was used to produce the carbonized and surface-modified carbons. The 106 μm 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 ($FeSO_4.7H_2O$), hydrogen peroxide H_2O_2 (30% W/V), H_2SO_4, sodium hydroxide NaOH, acetic acid (CH_3COOH), potassium dichromate ($K_2Cr_2O_7$), mercuric sulphate $HgSO_4$, silver sulphate Ag_2SO_4, manganese oxide, 10% HCl, potassium hydroxide 10% KOH (0.9 M), 10% (3.27 M) H_3PO_4, 2-(N,N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) (ii) kerosene and (iii) n-propanol and commercial activated carbon (Aqua Nucha).

Instrumentation: The instrument used was HI83099 COD and multiparameter photometer, HI 839800 COD reactor, COD test kits, COD standard reagents and set of titration equipment.

The COD was measured using Standard methods for water and wastewater Analysis, Part D5220, APHA (1995). The COD measurement instruments were supplied through an IFS Grant [Grant No: W5574-1] by the International Foundation for Science (IFS) Sweden.

Carbonization of Biomass: The dried Nipa palm biomass from the fronds were carbonized by taking about 25 ± 0.01 g of the Nipa palm leaves biomass (< 110 mesh size) and it 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 muffler 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 [6, 23, 24]. 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 [21]. The solids were then sun dried, followed by oven drying at 100°C for one hour [32] and then weighed. The dried sample was sieved through a 106-μm mesh Tyler sieve and the fractions < 106 μm 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 [31, 15, 39-40]. 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 ± 0.001 g Nipa palm leaves biomass was placed in a beaker containing 25 ml of 10% (3.27 M) H_3PO_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 [21, 6] 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 μm mesh Tyler sieve. Fractions < 106 μm were collected and kept in an air-tight container for use. Washing was complete when a pH of 7 ± 0.5 was ascertained [6, 13].

Basic Reagent Activated Carbon (BAC): 25 ± 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 [6, 21] 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 μm mesh Tyler sieve. Fractions < 150-μm were collected and kept in an air-tight container for use. Washing was complete when a pH of 7 ± 0.5 was ascertained [13, 18-19].

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 (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 (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 prepare the standards of kerosene by using the average density of kerosene (0.81 mg/cm³), the mass equivalent in each volume was calculated as in equation 1.

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

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 (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 mg/cm³), 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 (COD_i) and the COD of the distilled water was determined to give the blank COD.

Experimental Procedure for the set-up of Fixed Bed Column

Four fixed-bed columns were made of Pyrex glass with an internal diameter of 1.5 cm and 19.5 cm in height for the column studies. The bottom of the column was plugged with cotton wool and glass beads. The column was packed with carbons (PCC, AAC, BAC and CAC) followed by a layer of cotton wool and glass beads to provide uniform flow of solution.

Initially, two grams of adsorbent of 106 μm mesh particle size was added into the column and was shaken gently in order to have dense packing. This procedure was continued till a known quantity of the prepared adsorbent was packed in the column to yield the desired bed height of 7.62 cm containing 12.3 g of carbon.

After this, 500 mL of distilled water was gently passed through the packed bed column through a reservoir to make a more compact packing.

The COD of 100 mg/l solution of the SOCs solutions were determined to obtain the initial COD.

The SOCs solutions of concentration 100 mg/L at pH 6.5 were fed into the column from the top in a reservoir at the downward gravity flow rate of 15 mL/min and the effluent collected at the bottom at 30 minutes interval for 4 hours.

The aliquots of the SOCs effluent collected from the columns of PCC, AAC, BAC and CAC were then determined for COD levels. All experiments were carried out at ambient temperature.

To maintain pressure and constant flow rate, the SOCs solution in the overhead tank was maintained at a steady level by pouring solution from a second overhead reservoir tank containing stock solution of SOCs.

Determination of Chemical Oxygen Demand (COD) by Photometric Technique for Column Sorption Process.

a. Take 15 ml COD digestion tubes (pre-washed with dilute H_2SO_4) and add the following in sequence:
b. Exactly 2.50 ml sample was added to the Reagent vials and 2.50 ml of deionized water was added to another vial as blank.
c. Add 2.5 ml standard potassium dichromate digestion

reagent slowly and mix.

d. Add 3.5 ml sulfuric acid reagent through sides of the tubes and let it go to the bottom.

e. Cap and mix the contents (hand gloves were worn as contents are very hot) and cool.

f. Transfer tubes to the pre-heated COD digester at 150° C and digest for 2 hrs.

g. Invert each vial several times while still warm, then place them in test-tube rack.

h. Leave the vials in the tube rack to cool to room temperature. Do not shake or invert them anymore otherwise the samples may become turbid.

2.1. Method Selection

a) Turn the instrument on via the ON/OFF power switch

b) After 5 seconds of display, select the desired method of chemical oxygen demand

c) Place the COD vial adapter in the cuvette holder and ensure that the adapter is well fit inside.

d) Place the blank vial into the cuvette holder and push it down completely.

e) Press the zero key and the instrument will perform a zero sequence. If the zero sequence was successfully done, the display will be -0.0-. Now the meter is zeroed and ready for measurement.

f) Remove the blank

g) Place the sample vial into the holder and push it down completely

h) Press read and the instrument will perform the reading

i) The instrument displays the concentration in mg/L of oxygen demand

The optical system of COD instrument model HI 83099 is based on special subminiature tungsten lamps and narrow-band interference filters to guarantee both high performance and reliable results. Five measuring channels allow a wide range of tests.

2.2. Analysis of Experimental Data

Calculation of COD from Experimentation: The COD values of the respective solutions as displayed by the instrument is COD as mg O_2/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 by Eqn 2.

$$\% \text{ COD Removed} = \frac{COD_i - COD_f}{COD_i} \times 100 \quad (2)$$

Where COD_i = COD concentration of initial SOC working solutions before interactions with the carbons (mg/L) and COD_f = COD concentration of SOC working solutions after interactions with the carbons (mg/L).

Estimation of COD Reduction Capacity at Equilibrium

The apparent capacity of the carbons for COD reduction were examined at using the relationship expressed in eqn 3.

$$q_e = \frac{(COD_i - COD_f)V}{w} \quad (3)$$

Where q_e = COD reduction capacity (mg/g) of SOC removed at equilibrium, COD_i = COD concentration of SOC solution before interaction with the carbons (mg O_2//L). COD_f = COD concentration of SOC solution after interaction with the carbons (mg O_2/L). V = volume of SOC solution used (L) and w = weight of carbon (g).

Estimation of COD Reduction Capacity in Column Experiment: The column breakthrough curves was used to assess the loading behaviour of SOCs to be removed from solution in a fixed-bed column and is usually expressed as a function of time or volume of effluent for a given bed height [12, 14, 33-35, 41].

The column breakthrough capacity was calculated as in eqn 4:

$$q_b = \frac{Qt_b(C_o - C_b)}{m} \quad (4)$$

Where

q_b = breakthrough COD reduction capacity (mg g^{-1});

C_o and C_b are the initial and final SOCs concentration in the feed solutions (mgL-1);

Q = flow rate (Lmin-1);

t_s = service time (minutes); and

m = mass (grams) of the commercial activated carbon.

2.3. Estimation of Column Kinetic Model Parameters

The column experimental data in this project work was evaluated using the Adam-Bohart (also called bed-depth-service-time (BDST) model and Thomas models.

Adam-Bohart Kinetic Model: The time to breakthrough the column is modelled by service life of the bed. The service life of the bed can be determined using the bed-depth-service-time (BDST) model. The BDST model offers the simplest approach and rapid prediction of adsorber design and performance The BDST is a model for predicting the relationship between bed depths, X and service time t. This BDST model was focused on the estimation of characteristic parameters such as the maximum adsorption capacity (N_o) and kinetic constant (K). This model assumes that the adsorption rate is proportional to residual capacity of the sorbent and the concentration of the sorbing species. The service time was related to process conditions and operating parameters as presented in eqn 5 [37]:

$$\ln\left(\frac{C_o}{C_b} - 1\right) = \ln\left[\exp\left(\frac{K_{AB}xN_o}{Q} - 1\right)\right] - KC_o t \quad (5)$$

Where

t = service time of column under the above conditions also called time to breakthrough (min),

C_o = initial concentration of adsorbate (mg/dm^3),

C_t = final concentration of adsorbate at breakthrough value (mg/dm^3),

K_{AB} = Adam-Bohart rate constant (dm^3/mg/min) in fixed bed column

N_o = the fixed bed sorption capacity (mg/ dm^3)

x = the bed height of column (cm),

Q = the volumetric flow rate (dm^3/min).

The above equation can be written in the form of a straight line as presented in eqn 6:

$$t = \frac{N_o}{C_o F} x - \frac{1}{K_{AB} C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \quad (6)$$

The values of N_o and K_{AB} can be evaluated from the plot of t versus $\ln\left(\frac{C_o}{C_t} - 1\right)$

Thomas Kinetic Model: The Thomas model is one of the most general and widely used methods in column performance theory. The expression by Thomas for an adsorption column [37] is given as follows Eqn 7:

$$\frac{C_t}{C_o} = \frac{1}{1 + \exp[K_{Th}(q_o m - C_o V_{eff})/Q]} \quad (7)$$

Where
C_t is the effluent SOCs concentration (mg/L),
C_o, the inlet SOCs concentration (mg/L),
m, the mass of the adsorbent used (g),
V_{eff}, the effluent volume (ml),
Q, the flow rate (ml/min),
K_{Th} = Thomas rate constant (cm^3/mg/min)
q_o = maximum SOCs reduction capacity of the adsorbent (mg/g)

2.4. 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 by 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.

2.5. 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

3.1. Fixed-Bed Column COD Reduction Studies

Batch adsorption isotherm data does not give accurate scale-up for the real system [37]. Consequently, it is necessary to carry out fixed-bed continuous flow tests to obtain design parameters. In industry, a fixed-bed column is a type of immovable packed bed used to perform separation processes such as absorption, adsorption, stripping and chromatography. The main aim in designing adsorption column is to predict how much effluent the bed can treat or how long the bed will last before the regeneration is necessary. Column adsorption studies are very important because the process is simple to operate; generate experimental data necessary for scale-up of laboratory process to pilot production stage and also for optimization of the dynamic operational variables. In order to successfully design a column for adsorption process, it is necessary to conduct fixed-bed column experiments to generate these experimental data and model parameters. The continuous adsorption in fixed-bed column is often desired from industrial point of view. The performance of the packed bed is described through breakthrough curve. A successful design of column adsorption process is based on the prediction and evaluation of the breakthrough curve for effluent parameters. The times of the breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and dynamic response of any solute adsorption column.
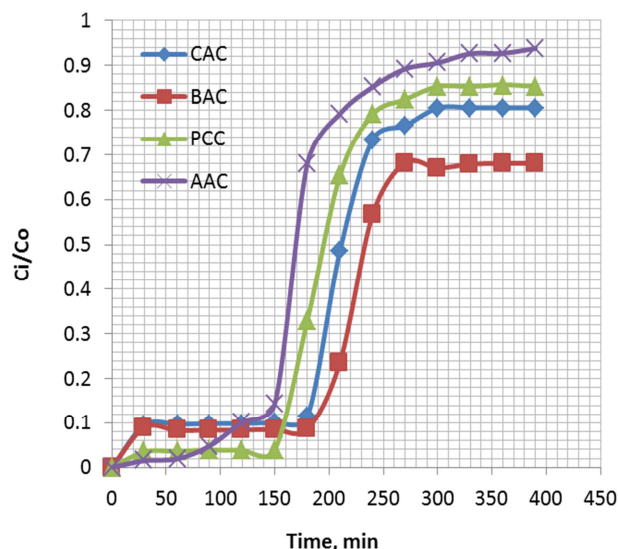
3.2. Breakthrough Curves

Based on the operational mode, adsorption can be generally classified into static adsorption and dynamic adsorption. Static adsorption, also called batch adsorption, occurs in a closed system containing a desired amount of adsorbent contacting with a certain volume of adsorbate solution, while dynamic adsorption usually occurs in an open system where adsorbate solution continuously passes through a column packed with adsorbent. For column adsorption, how to determine the breakthrough curve is a very important issue because it provides the basic but predominant information for the design of a column adsorption system. Without the information of the breakthrough curve one cannot determine a rational scale of a column adsorption for practical application. There are two widely used approaches to obtain the breakthrough curve of a given adsorption system: direct experimentation or mathematical modelling. The experimental method could provide a direct and concise breakthrough curve of a given system. However, it is usually a time-consuming and economical undesirable process, particularly for the trace contaminants and long residence time. Also, it greatly depends upon the experimental conditions, such as ambient temperature and residence time. Comparatively, mathematical modelling is simple and readily realized with no experimental apparatus required, and thus, it has attracted increasing interest in the past decades.

As an environmental chemist, both experimental technique and various mathematical models were applied in this research work to obtain the breakthrough curves. Breakthrough is defined as the point when a specified amount of the influent is detected in the effluent [37]. Prediction of the breakthrough curve for the effluent is the predominant factor for the successful design of a column adsorption process. The breakthrough time and the shape of the breakthrough curve are very important characteristics for the determination of dynamic response of the adsorption column. The breakpoint time is defined as the time of adsorption when the outlet concentration from the column was about 1 - 5% of the inlet concentration. The breakthrough curves provide idea on the early stage and exhaustion stage of the column.

The loading behaviour of material to be removed from solution in a fixed bed is usually expressed in terms of C_t/C_0 where (C_t = COD of effluent SOC concentration and C_0 = COD of influent SOC concentration in mg/ l). C_t/C_0 is then

plotted against time (t) in other to obtain the breakthrough curve. The curves are generally S-shaped, depicting a slow beginning, sharp increase and slow termination. Since there is no equilibrium in a column continuous process, the slow termination stage provides the exhaustion point of the bed.

The breakthrough curves for the COD reduction of DMABA by PCC, AAC, BAC and CAC at bed height 7.62 cm, flow rate 15 ml/min, influent concentration of 100 mg/L with a COD concentration of 88.4 mg O_2/L, pH 6.5 and temperature 30 ±1°C is depicted in figure 1.

Figure 1. Breakthrough curves for DMABA expressed as Ct/C0 versus time for different carbons at flow rate; initial COD of SOC (100 mg/L), influent pH 6.5, bed depth 7.62 cm and temperature 30 ±1°C.
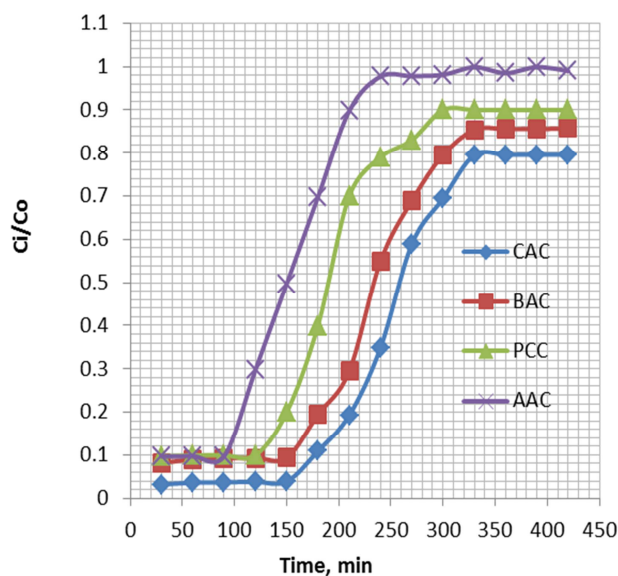
Figure 2. Breakthrough curves for kerosene expressed as C_t/C_0 versus time for different carbons at flow rate; initial COD of SOC (100 mg/L), influent pH 6.5, bed depth 7.62 cm and temperature 30 ±1°C.

As shown in the figure, the breakthrough time (t_b) for DMABA on PCC was 300 min, 170 min for AAC, 330 min for BAC and 362 min for CAC. Earlier breakthrough and exhaustion times were achieved for kerosene as revealed

from the breakthrough curves in figure 2.

The column breakthrough times (t_b) for kerosene on PCC, AAC, BAC and CAC were 190 min, 280 min, 235 min and 255 min respectively. The breakthrough curves for kerosene on the four carbons indicate that exhaustion time was not achieved at the maximum time of the experiment (that is 420 min.). This was due to a decrease in the residence time, which restricted the contact of kerosene solution to the carbons, therefore the kerosene molecules did not have enough time to diffuse into the pores of the carbon and they exited the column before equilibrium occurred. The lower breakthrough time may be because the binding sites became more quickly saturated in the column due to different types of large molecules found in kerosene. As depicted by figure 3, the breakthrough time varied with the different carbons employed. The periods of time for the COD reduction for n-propanol to reach approximately 50% breakthrough, i.e., $C_t/C_o = 0.5$ for PCC, AAC, BAC and CAC were 195 min, 150 min, 210 min and 323 min respectively.
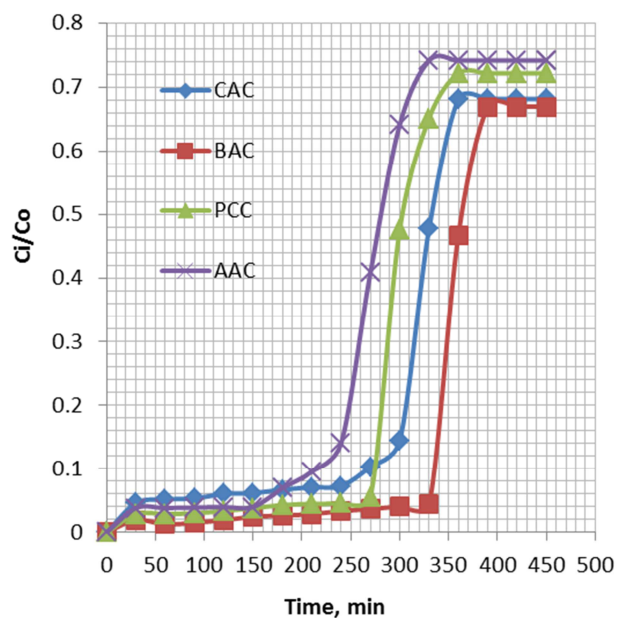
Figure 3. Breakthrough curves for n-propanol expressed as C_t/C_0 versus time for different carbons at flow rate; initial COD of SOC (100 mg/L), influent pH 6.5, bed depth 7.62 cm and temperature 30 ±1°C.

3.3. COD Reduction Capacity of the Column

Estimation of the COD column reduction capacity is an important factor in the design of column adsorption process. The reduction capacity was obtained by using the analysis of fixed-bed column data. The column breakthrough times (t_b) for the SOCs were then derived from the breakthrough curves and employed in the computation of the breakthrough COD reduction capacity (q_b), effluent volume (V_{eff}), the total quantity of SOC in the column q_{tot}, the total amount of SOC sent to the column m_{tot}, unadsorbed amount of SOC in the column (C_e), the column performance (% total SOC reduction capacity), and the maximum column SOC reduction capacity (q_e).

The computed process parameters for DMABA on the three Nipa palm and commercial carbons are presented in Table 1.

Table 1. Column parameters for SOCs obtained for different carbons at flow rate; initial SOC concentration (84 mg/L), influent pH 6.5, bed depth 7.62 cm and temperature 30 ±1°C.

Carbons	DMABA			Kero			N-P		
	q_e	q_b	% R_{COD}	q_e	q_b	% R_{COD}	q_e	q_b	% R_{COD}
CAC	16.74	4.83	68. 90	16.74	4.83	49.01	43.71	12.59	68. 90
BAC	15.26	4.39	62.81	15.26	4.39	31.87	28.42	8.19	62.81
PCC	13.88	3.99	57.099	13.88	3.99	29.59	26.39	7.60	57.09
AAC	12.95	3.73	53.29	12.95	3.73	25.80	23.01	6.63	53.29

Key: q_b = breakthrough COD reduction capacity (mg g^{-1})

q_e = maximum column capacity (mg g^{-1})

% R_{COD} = Percent Column COD reduction

The data showed that, the total quantity of DMABA adsorbed in the column for a feed concentration of 100 mg/l and flow rate of 15 ml/min by PCC, AAC and BAC were 49.58 mg, 46.62 mg and 54.95 mg respectively. These values are comparable to the total quantity of DMABA adsorbed in the column by the commercial carbon (68.9 mg). The column adsorption capacity of DMABA by PCC, AAC and BAC were 13.88 mg/g, 12.95 mg/g and 15.26 mg/g corresponding to total percent COD reduction of 57.10%, 53.29% and 62.81%. The data revealed that BAC had the highest COD reduction capacity in the column.

Total quantity of kerosene in the column after a total of 100.08 mg has pass through the column at flow rate of 15 ml/min were 16.25, 12.83 and 20.09 mg for PCC, AAC and BAC respectively. The data in Table 1 reveals that among the Nipa palm carbons, BAC had the highest adsorption capacity and total removal of 5.58 mg/g and 20.08% respectively.

The adsorption capacities and total quantity of kerosene removal by the other Nipa palm carbons were PCC (4.51 mg/g; 16.23%) and AAC (3.56 mg/g; 12.82%). The breakthrough curves are dispersed. This might be due to slow COD reduction kinetics of kerosene on the carbons.

The column data parameter for n-propanol obtained for different carbons at flow rate15 (ml/min); initial COD of SOC (100 mg/L), influent pH 6.5, bed depth 7.62 cm and temperature 30 ±1°C are presented in Table 1. The data demonstrates that the total COD reduction capacity in the column for n-propanol was highest for BAC (31.87%) among the Nipa palm derived carbons and is comparable to CAC (49.012%).

Column Kinetic COD Reduction Study

There are a number of mathematical models for the evaluation of efficiency and applicability of adsorption columns for large scale operations. They include Adam-Bohart, Wolborska, Thomas, Clark, and Yoon-Nelson models. However, in this research work, the Adam-Bohart and BDST models were used to analyze the behavior of the adsorbate-adsorbent system in the column.

Adam-Bohart Model

The prediction of column performance is carried out using the well-known Adam-Bohart model [22, 42] also called the Bed Depth Service Time (BDST) model.

The fundamental Adam-Bohart equations describing the relationship between normalized concentrations (C_t/C_0) and time (t) in a flowing fixed bed system was used to describe the kinetics in this research work. This model assumes that the adsorption rate is proportional to both the concentration of the adsorbing species and the residual capacity of the adsorbent towards targeted adsorbate species.

The final design equation of the Adam-Bohart model used to evaluate the data in this research work is presented in equation 6.

A plot of $\ln \left(\frac{C_o}{C_t} - 1 \right)$ against time (t) (Eqn 6) was used to calculate the values of N_o and K_{AB} for the COD reduction of the SOCs by Nipa palm carbons and the commercial carbon.

The plots for DMABA, kerosene and n-propanol are presented in figures 4, 5 and 6.
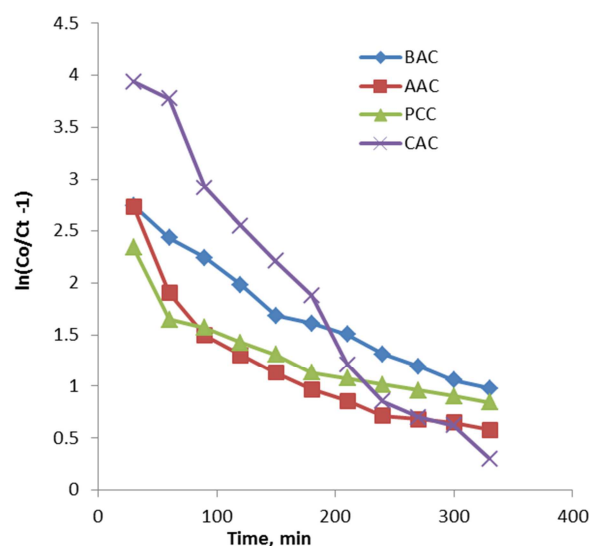
Figure 4. Adam-Bohart kinetic plot for the COD reduction of DMABA solution by PCC, AAC, BAC and CAC.

The column kinetic parameters for DMABA as presented in Table 2, showed that the Kinetic constant K_{AB} for COD reduction of PCC, AAC, BAC and CAC in the column were 0.0076 (L/mg/h), 0.0024 (L/mg/h), 0.0036 (L/mg/h) and 0.0034 (L/mg/h) respectively. The COD reduction capacity also called adsorption capacity, N_o, in the column for DMABA as obtained from the Adam-Bohart kinetic model plot was 10.16 mg/cm^3 for PCC, 9.02 for mg/cm^3 for AAC, 12.44 mg/cm^3 for BAC and 13.33 mg/cm^3. The results indicate that N_o is highest for BAC and is comparable to that of the commercial carbon. As for the r^2, the values show distribution between 0.838 and 0.997.

Nevertheless, most of the r^2 values are greater than 0.9, which indicates that the data fits into the model perfectly. As a result, it can be confirmed that the Adam – Bohart model is

suitable to explain the overall adsorption kinetics of DMABA in the column containing the three Nipa palm derived carbon and they are comparable to the commercial carbon. The r^2 value for DMABA by all the carbons are greater than 0.95 except AAC.
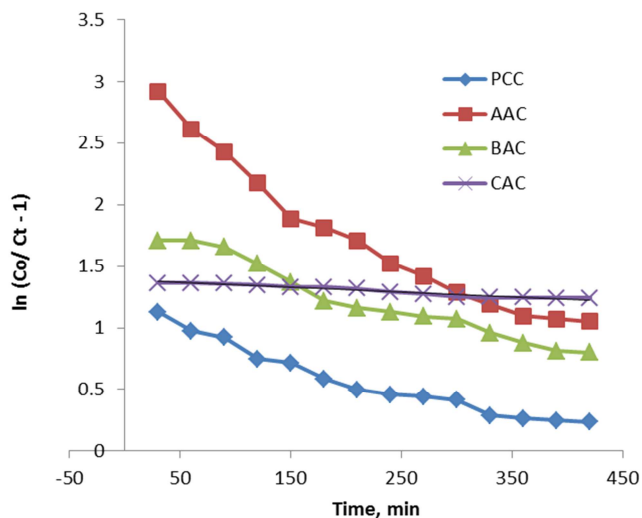

Figure 5. *Adam-Bohart kinetic plot for the COD reduction of kerosene solution by PCC, AAC, BAC and CAC.*

The Adam-Bohart parameters for kerosene as derived from the plot of figure 5 are presented in Table 2. The data showed that K_{AB} for COD reduction of kerosene by AAC (0.0028, L/mg/h) and BAC (0.0028, L/mg/h) are the same in the column, while for PCC it was 0.00138 L/mg/h. The COD elimination capacity for kerosene in the column containing the three Nipa palm carbons and the commercial carbon was also estimated. It was found the COD reduction capacity, N_o, for PCC, AAC, BAC ad CAC were 12.95 mg/cm³, 10.52 mg/cm³.
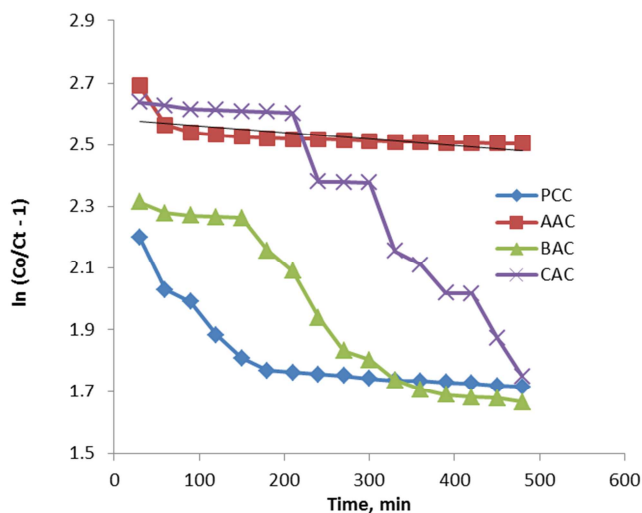

Figure 6. *Adam-Bohart kinetic plot for the COD reduction of n-propanol solution by PCC, AAC, BAC and CAC.*

Also for kerosene, the value of N_o is highest for BAC than the other Nipa palm derived carbons and this value is comparable to that of the commercial carbon. The coefficient

of determination, r^2, values for COD reduction of kerosene by the carbons show that all the r^2 values are greater that 0.94, which is an indication of good fit of kerosene data to the Adam-Bohart kinetic model.

From the Adam-Bohart kinetic model plot (Figure 6), all column kinetic parameters were evaluated are presented in Table 2. The results indicate that COD reduction in the column containing PCC, AAC, BAC and CAC have coefficient of determination, r^2, values distributed between 0.094 and 0.997. Since most of the r^2 values are greater than 0.90, which indicates that the data for n-propanol also completely fits into the model. The COD reduction capacity of the column containing the three Nipa palm carbons and the commercial carbon ranged between 66.7 and 15.16 L/mg/h.

The entire results confirmed that the Adam – Bohart model is suitable to explain the overall adsorption kinetics of the SOCs in the column containing the three Nipa palm derived carbon and they are comparable to the commercial carbon.

Table 2. *Calculated column kinetic parameters from Adam-Bohart model kinetic plot for COD reduction of SOCs by Nipa palm derived carbons and the commercial carbon.*

| SOCs | Carbons | Column Model Parameters | | |
| | | Adam-Bohart Parameters | | |
		K_{AB} L/mg/h	N_o mg/cm³	r^2
DMABA	PCC	0.00762	10.156	0.969
	AAC	0.0024	9.024	0. 838
	BAC	0.0036	12.442	0.998
	CAC	0.00342	13.333	0.997
Kerosene				
	PCC	0.00138	12.951	0.943
	AAC	0.00282	10.516	0.945
	BAC	0.0028	16.649	0.9963
	CAC	0.0024	19.630	0.9964
n-propanol				
	PCC	0.0011	9.568	0.927
	AAC	0.0012	6.651	0.904
	BAC	0.0014	13.903	0.995
	CAC	0.0018	15.160	0.997

3.4. The Thomas Model

The Thomas model is one of the most general and widely used methods in column performance theory. The linear form of Thomas model [42, 22] as given in equation 7 was used to evaluate the maximum COD reduction capacity of the SOCs (mg/g). Thomas model has been used by many researchers to study packed bed adsorption kinetics [36, 16, 38]. The kinetic coefficient, K_{Th} and the adsorption capacity of the bed, q_o were determined from the plot of $In[(C_t/C_o)-1]$ against t (Figures 7, 8 and 9). The results of K_T, r^2 and q_o are given in Table 3. Thomas rate constant, K_T for COD reduction of DMABA in the PCC column was 0.0435 mL/min.mg, while that of AAC and BAC columns K_T were 0.128 and 0.059 mL/min.mg respectively. The maximum COD reduction capacity, q_o for DMABA solutions by the Nipa palm carbons and the commercial carbons were 11.81 mg/g (PCC), 10.62 mg/g (AAC), 19.78 mg/g (BAC) and 21.99 mg/g (CAC) respectively.
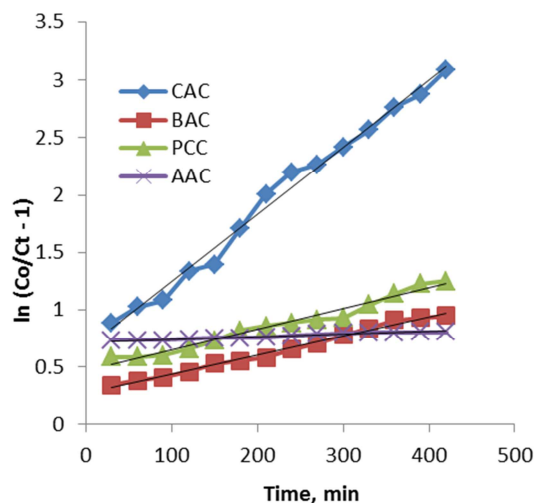
Figure 7. Thomas kinetic plots for COD reduction of DMABA solution by PCC, AAC, BAC and CAC.
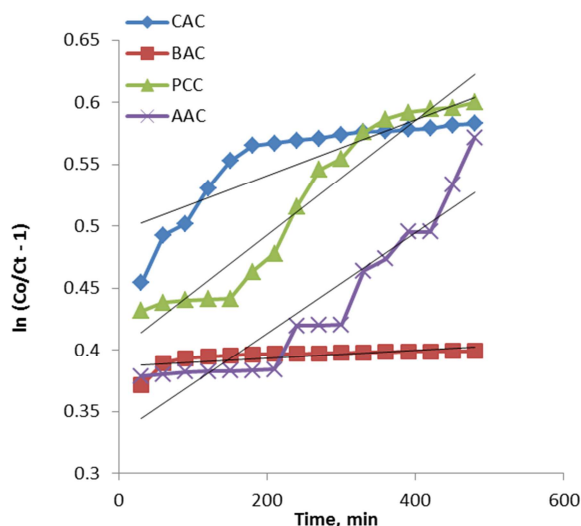

Figure 8. Thomas kinetic plots for COD reduction of kerosene solution by PCC, AAC, BAC and CAC.
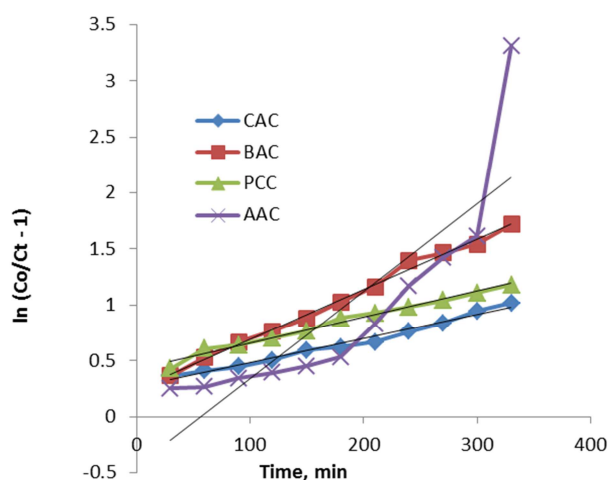

Figure 9. Thomas kinetic plots for COD reduction of n-propanol solution by PCC, AAC, BAC and CAC.

High values of determination coefficients r^2 were determined indicating that the kinetic data conformed well to

Thomas model in contrast with the report of Sivakumar and Palamisamy (2009) but in agreement with the results obtained by Baek [16].

Experimental results for COD reduction of aqueous solutions of kerosene by the commercial and Nipa palm derived carbons were also fitted into the Thomas model equation and plotted (Figure 8) to generate the Thomas model kinetic parameters, which are depicted in Table 3, which shows that the maximum column COD reduction capacity for kerosene among the three Nipa palm derived carbon was BAC with a value of 15.54 mg/g. When this value was compared with the commercial carbon with a value of 16.64 mg/g, it could be suggested that, the BAC is as good as CAC in the reduction of kerosene in the fixed bed column.

The coefficient of determination values show that all r^2 values are > 0.95, indicating a very good fit to the Thomas model. The data obtained for n-propanol from the experiment were fitted to the Thomas model equation. From the analysis, the Thomas rate constant (K_{Th}) and the equilibrium COD reduction capacity (q_o) were deduced from the plot (Figure 9) and the column parameters presented in Table 3. The data showed that the Thomas rate constant, K_T ranged from 0.20 to 0.050 for the Nipa palm derived and commercial carbons, while the maximum column COD reduction capacity for n-propanol for the Nipa carbons ranged between 10.16 – 16.20 mg/g. The maximum column COD reduction capacity for the commercial carbon was 24.42 mg/g. The r^2 values were 0.47, 0.87, 0.94 and 0.987 for PCC, AAC, BAC and CAC. These values validate the use of Thomas model to predict the maximum COD reduction capacity for n-propanol of BAC and CAC beds, while the model is not applicable to that of the beds containing AAC and PCC.

Table 3. Calculated column kinetic parameters from Thomas model kinetic plot for COD reduction of SOCs by Nipa palm derived carbons and the commercial carbon.

SOCs	Carbons	Column Model Parameters		
		Thomas Parameters		
		K_{TH} L /min	q_o mg/g	r^2
DMABA	PCC	0.0435	11.814	0.985
	AAC	0.0128	10.615	0.727
	BAC	0.0222	19.777	0.995
	CAC	0.0455	21.994	0.980
Kerosene				
	PCC	0.0556	10.302	0.972
	AAC	0.0500	7.532	0.955
	BAC	0.0588	15.542	0.990
	CAC	0.0172	16.641	0.999
n-propanol				
	PCC	0.0500	12.095	0.871
	AAC	0.0333	10.159	0.469
	BAC	0.0250	16.200	0.935
	CAC	0.0200	24.415	0.987

4. Conclusions

COD reduction experiments were conducted in a fixed-bed column and the results show that, the optimum performance (mg cm^{-3}) of the carbons are 10.16 (PCC), 9.024 (AAC) and

12.442 (BAC) for DMABA; 12.95 (PCC), 10.51 (AAC) and 16.64 (BAC) for kerosene and 9.568 (PCC), 6.651 (AAC) and 13.903 (BAC) for n-propanol) respectively. Amongst the Nipa palm carbons, the breakthrough time for BAC was longer than the PCC and AAC. The longer the breakthrough time, the more time the material spends on the carbon in a column and the better the removal of the material. Hence, BAC is adjourned to be of a better efficiency than PCC and AAC. 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. 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. Furthermore, chemical modification has been shown to play a significant role in enhancing the physicochemical properties of the Nipa derived carbons and that Nipa palm leaves are a dependable source for the production of low-cost, locally accessible, and eco-friendly adsorbents as a good substitute to the existing adsorbents for removing organic contaminants in wastewater. Therefore, Nipa palm is potentially a useful mangrove species in the Niger Delta area of Nigeria and efforts should be made at non-eradication of the plant.

Acknowledgments

Conflicts of Interest

The authors declare no conflicts of interest.

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