Chemical Oxygen Demand (COD) Attenuation of Methyl Red in Water using Biocarbons obtained from Nipa Palm Leaves

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ABSTRACT: Attenuation of methyl red dyestuff in water was assessed by COD reduction after contacting the solution with biocarbons produced by one-pot pyrolysis of sopping Nipa palm leaf biomass in H_2O (physically-modified biocarbon: PMB), H_3PO_4 (acid-modified biocarbon: AMB) and KOH (base-modified biocarbon: BMB). Physicochemical characterization of the biocarbons were investigated and the result for BMB were carbon yield (46.6 ± 0.21 %), porosity (79%), iodine number (814 mg/g), surface area (681 m^2/g) and pH (6.41 ± 0.11 to 7.81 ± 0.12). Optimal COD reduction for methyl red in water by PMB, AMB, BMB compared with CAC were 82.7%, 76.7 %, 83.5 %, and 93.3 % respectively. Langmuir isotherm model was used to predict the maximum COD reduction capacity of the biocarbons and CAC (PMB: 2.15 mg/g, AMB: 8.73 mg/g, BMB: 11.83 mg/g and CAC: 62.60 mg/g). Thermodynamic assessment of the data based on Gibb's free energy (ΔG^o) revealed that ΔG^o values were negative (- 1.31 to - 5.89 kJ/mol) and relatively low (<< -20 kJ/mol), which indicated spontaneous nature requiring minimal energy. One-way analysis of variance (ANOVA) performed to validate the COD degradation capacity for methyl red in water amongst the biocarbons revealed no significant difference (p > 0.05). Conclusively, Nipa palm could be a favorable source to derive eco-friendly and locally accessible biocarbon for mitigation of organic contaminants in water. ©JASEM

Attenuation of chemical oxygen demand (COD) as index of measurement to evaluate the degree of organic contaminant elimination in water is a low cost and viable option for low developing countries. This is because COD measurement is fast, reliable, accurate and simple in the face of expensive modern instrumentation.

Contamination of water resources by dye pollutants such as methyl red has serious environmental implications, due to their toxicity, high COD, and nasty appearance. Therefore, releasing such contaminants into the aquatic ecosystem without competent management is unwelcomed (Adowei *et al*., 2015, Abechi *et al*., 2013, Tarawou *et al*., 2010, Horsfall *et al.,* 2007, Birhanli and Ozmen 2005).

Clothing and paper industries produce wastewater with numerous constituents that contains large amount of dyes, which may be difficult to treat (O'Neill *et al.,* 2000). Conventional methods of treating dye laden wastewater which includes biological oxidation, chemical oxidation, photo-degradation, coagulation and reverse osmosis are expensive (Ekpete and Horsfall, 2011, Ekpete *et al.,* 2011, Tsai *et al.,* 2001). However, in recent times, an extensive diversity of low priced materials has been employed. They include agricultural by-product such as waste coir pith (Kadirvelu *et al.,* 2000), Indian rosewood sawdust (Namasivayam *et al.,* 2001), Fluted Pumpkin Wastes (Horsfall and Spiff 2005, Ekpete and Horsfall, 2011, Ekpete *et al.,* 2011a, Ekpete *et al.,* 2011b), *Rhizophora mangle* Aerial Root Waste (Horsfall *et al*., 2005), almond tree leaves waste (Horsfall and Vicente, 2007), Wild Cocoyam Biomass (Horsfall and Spiff, 2005) Cassava Waste Biomass (Horsfall and Abia, 2003) However, these biomaterials do not have the capacity to withstand the harshness of wastewater and many researchers have turned to converting the biomaterials into activated carbon as alternative low cost materials (Ahmad *et al.,* 2010, Tarawou *et al.,* 2010a,b,c, Ahmad and Hameed, 2009, Adinata *et al*., 2007, Ahmedna *et al*., 2000).

Nipa palm (*Nypa Fruiticans* Wurmb) belongs to the family Palmae or Arecaceae (Mohamad *et al.,* 2014) that propagates along muddy and especially soft banks of brackish inter-tidal area of rivers. In the Niger Delta area of Nigeria, Nipa palm plant is speedily attacking the mangrove forest and eventually interchanging with the important floral species such as *Rhizophora spp*. and *Avicennia Africana*. These two mangrove species offer the indigenous people with fuel-wood, fishing poles, tannin and provide excellent environment for shelter, nurseries and breeding grounds for fish, periwinkles, crabs, oysters and clams. This threat to the important mangrove floral species by Nipa palm is a source of distress because locals depend on these species for their socio-economic wellbeing (Adowei *et al*., 2014, Wankasi *et al.,* 2005).

Therefore, the aim of this work was to transform leaves of Nipa palm into differentially modified biocarbons via a one-pot pyrolysis and their subsequent use for evaluating COD reduction of methyl red in water.

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MATERIALS AND METHODS

Sample Collection: Collection of Nipa palm plant was done at the inter-tidal flats of Ogbunabali waterfront in Port Harcourt, Rivers State, Nigeria (Figure 1) with coordinates of 4°49′27″N 7°2′1″E and 4.82417°N 7.03361°E respectively and taken to the herbarium laboratory for taxonomic classification.

Sample Preparation: Fresh Nipa palm fronds were carefully removed from the stalks and washed with sufficient water to remove surface filth and sun dried, followed by oven drying at 110 °C for several days. Dried leaves were grounded using a grinder (Landa Cisa 2D) to a fine powdered biomass and sieved with mesh size 106 µm.

List of Chemicals: The major reagents used include: ferrous ammonium sulphate (FAS), ferroin indicator, iron (II) sulphate heptahydrate ($FeSO_4.7H_2O$), hydrogen peroxide (H_2O_2: 30 % W/V), sulphuric acid (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 (MgO), hydrochloric acid (HCl: 10 %), potassium hydroxide (KCl: 10 % , 0.9 M), phosphoric acid (H_3PO_4: 10 %, 3.27 M), methyl red sodium salt ($C_{15}H_{14}N_3NaO_2$) and commercial activated carbon (AquaNucha).

Fig 1: Map of Africa (with Nipa palm insert) collected at Ogbunabali waterfront, Rivers State, Nigeria

Production of Physically Modified Biocarbons
Production of physically modified biocarbons has been published elsewhere (Adowei, et al, 2015, Itodo *et al.,* 2009, Turoti *et al*., 2007, Gimba *et al.,* 2004 and Fan *et*

al., 2003). Briefly, a 1:1 ratio of Nipa palm leaves biomass and water was carefully made. The paste was heated to 500 °C for 10 min and left in the oven for 2 hr, and poured into a bowl containing some ice block crystals. Excess water was drained and the paste dried at ambient temperature to give physically modified biocarbon (PMB). To eliminate surface ash and remove residual acid, PMB was thoroughly washed with 10% HCl and sufficient hot water, followed by oven drying to constant weight and sieved through < 106 µm sieve.

Production of Acid and Base Modified Biocarbons
Carbonized biocarbon was modified into two sets of biocarbons according to the methods of Ahmedna *et al.,* 2000, Ash *et al.,* 2006 and Sugumaran and Seshadri, 2009,) with slight modifications. The modified biocarbons were (i) Acid modified biocarbon (AMB) and (ii) Base modified biocarbon (BMB). Briefly, AMB and BMB were made by sopping some Nipa palm leaves biomass in 10 % (3.27 M) H_3PO_4 and 10 % (0.9 M) KOH solutions respectively with careful mixing to form pastes, which were heated to 500 °C within 10 min, cooled to room temperature and weighed. The biocarbons formed were thoroughly washed with 10% HCl and plenty of hot water (complete washing was achieved at pH 7 ± 0.5), followed by oven drying to constant weight and sieved through < 106 µm sieve.

Commercial Activated Carbon (CAC): A top wood-based activated carbon with trade name AquaNuchar SA-1500 was purchased and used as the control.

Experimental Procedures for Physicochemical Characterization: Some physicochemical physiognomies which affect biocarbon surface properties were evaluated.

Biocarbon Yield: The percent biocarbon yield was calculated by applying eqn.1 (Cui *et al.,* 2007).

$$x(\%) = \frac{m}{m_o} \text{ x } 100………………..1$$

Where x = biocarbon yield (%), m = mass of biocarbon (g) and m_o = mass of raw sample (g).

Attrition: Biocarbon attrition was determined by wet attrition method of Toles *et al*., 2000 with slight modification which has been published elsewhere (Adowei, et al., 2015).

pH: Determination of biocarbon pH was done by standard method - ASTMD3838-80 (AOAC, 1999) with slight modification which has been published elsewhere (Adowei *et al.,* 2015).

Ash Content: Evaluating biocarbon ash content was achieved by standard method number ASTM D2866-94 (AOAC, 1999) with slight modification which has been published elsewhere (Adowei, et al., 2015).

Moisture Content: Thermal drying method (Rengaraj *et al*., 1999) was used for determination of moisture content with slight modification which has been published elsewhere (Adowei *et* al., 2015).

Iodine Number: Sodium sulphate titration method as reported by Madu and Lajide (20135) was used to determine iodine number of biocarbons with slight modification which has been published elsewhere (Adowei *et al*., 2015).

Porosity: Biocarbon penetrability was evaluated as given by Aziza *et al*., (2008) with slight modification.

Surface Area: Sears' method (Sears, 1956) as modified by Alzaydien (2009) was used to measure the surface area of the biocarbons.

Standard Methyl Red Solutions: 1.0 g water soluble Na-salt of methyl red crystals were weighed to make a stock solution of 1000 mg/l. Working methyl red solutions with concentrations (mg/l) of 20, 40, 60, 80, and 100 were then prepared.

Biocarbon Dosage Determination: 0.2, 0.4, 0.6, 0.8, and 1.0 g of each biocarbons and CAC were weighed into several 150 ml plastic sample containers followed by addition of 50 ml methyl red (100 mg/l) solution, covered firmly and agitated for 1 hour at 150 rpm, thereafter, the suspensions were allowed to stand on the bench for 30 min, centrifuged at 2000 rpm for 2 min to obtain clear supernatant solutions for analysis of final COD (COD_f).

Initial Concentration Determination: 2.0 g of each biocarbons and CAC were weighed into several 150 ml plastic sample containers followed by addition of 50 ml methyl red with the following concentrations (mg/l): 20, 40, 60, 80, and 100, covered firmly and agitated for 1 hour at 150 rpm. Thereafter, the suspensions were allowed to stand for 30 min, centrifuged at 2000 rpm (2 min) to obtain clear supernatant solutions for final COD (COD_f) analysis.
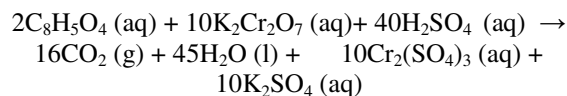
Initial pH Determination: 2.0 g of each biocarbons and CAC were weighed into several 150 ml plastic sample containers followed by addition of 50 ml methyl red with concentration (100 mg/l), covered firmly and agitated for 1 hour at 150 rpm. The pH values of these suspensions were adjusted to 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0 by adding either conc. HCl or NaOH. The suspensions were allowed to stand for 30 min, centrifuged at 2000 rpm for 2 min to obtain clear supernatant solutions for analysis of final COD (COD_f).
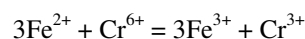
Reflux Time Determination: 2.0 g of each biocarbons and CAC were weighed into several 150 ml plastic sample containers followed by addition of 50 ml methyl red solution with concentration (100 mg/l), covered firmly and agitated for 1 hour at 150 rpm. The pH value of the suspensions were adjusted to 6.0 by adding either conc. HCl or NaOH. The containers were labelled for different refluxing time interval of 10, 20, 30, 40, 50, 60 minutes. At the end of each time interval, the suspensions were allowed to stand for 30 min, centrifuged at 2000 rpm for 2 min to obtain clear supernatant solutions for analysis of final COD (COD_f).

COD Reduction Determination: The two-step process of Waynes (1997) was adopted to determine the COD reduction of the methyl red solution by biocarbon.

First Step: This is the digestion step where organic matter is oxidized by dichromate ions in sulphuric acid to CO_2 and H_2O. During heating the dichromate ions ($Cr_2O_7^{-2}$) form orange-colored solutions.

$$2C_8H_5O_4 \text{ (aq)} + 10K_2Cr_2O_7 \text{ (aq)} + 40H_2SO_4 \text{ (aq)} \rightarrow 16CO_2 \text{ (g)} + 45H_2O \text{ (l)} + 10Cr_2(SO_4)_3 \text{ (aq)} + 10K_2SO_4 \text{ (aq)}$$

Second Step: During titration, ferrous ammonium sulphate (FAS) reacts with dichromate ion to form green coloured chromic ion solution. After the end point, FAS reacts with the indicator to form brown colour solution as depicted below.

$$3Fe^{2+} + Cr^{6+} = 3Fe^{3+} + Cr^{3+}$$

To determine the COD of each sample, 10 ml 0.125 M $K_2Cr_2O_7$ solution was added to 20 ml clear supernatant solution in 250 ml round-bottom flask followed by addition of 1.0 g silver sulphate and drop-wise addition of 40 ml conc. sulphuric acid with gentle swirling until complete dissolution of silver sulphate occurs. Anti-bumping aid were added to the flask and a reflux condenser connected. The mixture was gently refluxed for 10 min or more as the case may be, after which its content was cooled. 50 ml distilled water was flushed through the condenser, and the cooling completed under running tap water. 2 drops of ferro in indicator solution

was added and the subsequent mixture titrated with standardized 0.025 *M* FAS solution until a change in colour from yellow-green via blue-green to reddish brown was observed, which indicated the end-point. 20 ml distilled water as blank was also taken through the same process.

*Analysis of Experimental Data: Quantification of COD Reduction***:** COD attenuation for the various solutions and blanks were quantified as presented in eqn. 2.

$$\text{COD as mg O}_2/l = \frac{(V_A - V_B) \text{ x m x } 8000}{V_S} \quad \dots\dots\dots\dots 2$$

Where V_A = volume of FAS used for blank (ml); V_B = volume of FAS used for sample (ml); M = molarity of FAS; V_s = Volume of sample used (ml) and 8000 = milli-equivalent weight of oxygen x 1000 ml/*l*.

*Evaluation of % COD Reduction***:** This was calculated after quantifying the COD attenuated for initial and final solutions as presented in Eqn. 3.

$$\% \text{ COD Removed} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \text{ x } 100 \quad \dots\dots\dots\dots 3$$

Where COD_i = COD for initial methyl red solutions before interactions with biocarbons (mg/*l*) and COD_f = COD for methyl red solutions after interactions with biocarbons (mg/*l*).

Evaluation of COD Reduction Capacity at Equilibrium
The apparent capacity of biocarbons and CAC for COD reduction were examined using the relationship expressed in eqn. 4.

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

Where q_e = COD reduction capacity (mg/g) of methyl red at equilibrium, COD_i = COD for methyl red solution before interaction with biocarbons (mg O_2//*l*). COD_f = COD for methyl red solution after interaction with biocarbons (mg O_2/*l*). V = volume of methyl red solution used (*l*) and w = weight of biocarbon used (g).

*Evaluation of Equilibrium Data***:** COD reduction experimental data were evaluated with Langmuir and Freundlich isotherm models

Langmuir isotherm model was employed to estimate the maximum reduction capacity and the linear expression is stated in eqn. 5.

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

Where K_L = Langmuir constant (*l* mg^{-1}) and q_{max} = maximum COD reduction (mg/g), C_e = equilibrium COD reduction and q_e = COD reduction capacity (mg/g).

Plot of C_e/q_e against C_e is expected to give linear graph with slope = $1/q_{max}$ and interception = K_l/q_{max}.

Freundlich isotherm model was used to estimate the degree of COD reduction. The linear form of this equation is given in eqn. 6.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \dots\dots\dots\dots 6$$

To determine the constants K_F and *n*, plot of $\log q_e$ against $\log C_e$ is expected to be linear. The slope = $\frac{1}{n}$ and intercept = $\log K_F$.

Evaluation of Favorability of COD Reduction: The favourability of COD degradation of methyl red in water was predicted using the separation factor as presented (S_F) in eqn. 7.

$$S_F = \frac{1}{1 + K_L C_o} \quad \dots\dots\dots\dots 7$$

Where S_F = favourability factor, C_o = initial methyl red concentration and K_L = Langmuir constant.

Kinetic Model Analysis of COD Reduction
Pseudo-first and - second order kinetic behaviors were examined using COD reduction experimental data obtained from refluxing time-dependent analysis.

Pseudo – First Order Kinetics: The linear pseudo – first order kinetic model shown in eqn. 8 was used

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)t \quad \dots\dots 8$$

Where q_e = COD reduction capacity (mg/g), q_t = COD reduction capacity of methyl red in water at any time t (mg/g), k_1 = pseudo-first order rate constant (min^{-1}) and t = time (min).

Plotting computed values of $\log (q_e - q_t)$ against t (min) is expected to give a linear graph to enable the computation of slope (q_e) and intercept (k_1).

Pseudo – Second order Kinetics: Ho and co-workers (1995) proposed a linear equation to measure the

pseudo-second-order kinetic rate which is shown in eqn. 9.

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e} \ldots\ldots\ldots\ldots\ldots .9$$

Where q_e = COD reduction capacity (mg/g), q_t = COD reduction capacity of methyl red in water at any time t (mg/g), k_2 = pseudo-second-order rate constant (g/mg. min), t = time (min), h_o = initial COD reduction rates (mg/g. min).

If $\frac{t}{q_t}$ is plotted against t, a straight line graph is likely to be obtained, with slope and intercept that may be used to calculate the initial COD reduction rate and the pseudo-second-order rate constants.

Thermodynamic Analysis of COD Reduction: The apparent Gibbs free energy was obtained using eqn. 10.

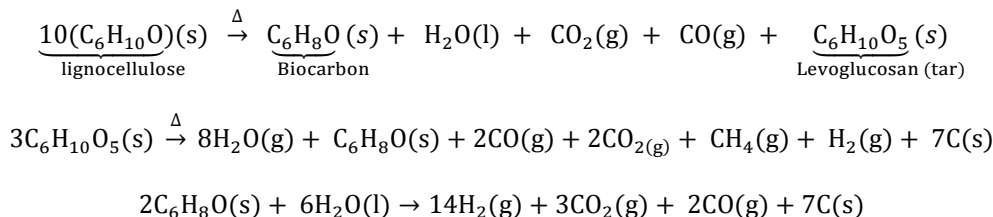$$\Delta G^0 = -RT \ln K_L \quad \ldots\ldots\ldots\ldots ..10$$

Where K_L = thermodynamic equilibrium constant of the Langmuir model.

Analytical Precision and Quality Control: Careful quality control measures such as washing of glassware, use of analytical grade reagent, use of freshly preparing working standards, reagents and blanks, and comparing analytical procedures by use of commercial activated carbon (AquaNucha) were appropriately adopted.
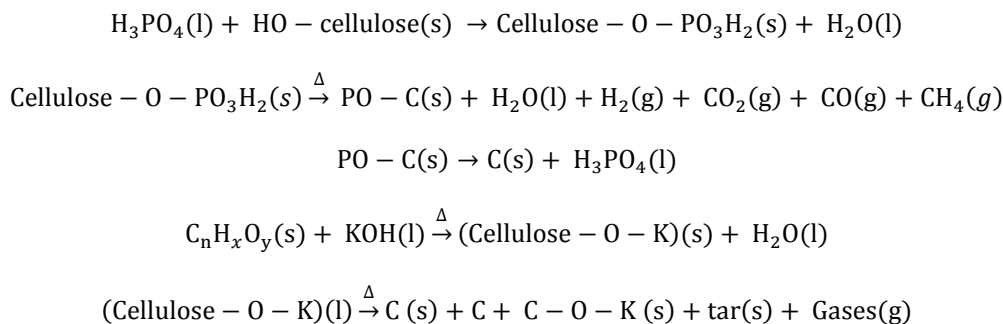
Statistical Analysis of Experimental Data: The consistency of COD attenuation data were done making triplicate analysis and computation of mean, standard deviations, standard errors and analysis of variance (ANOVA).

RESULTS AND DISCUSSION
Biocarbon production from the biomass was achieved by pyrolysis in an inert atmosphere and the resultant series of chemical reactions are illustrated as.

$$\underbrace{10(C_6H_{10}O)(s)}_{\text{lignocellulose}} \xrightarrow{\Delta} \underbrace{C_6H_8O\,(s)}_{\text{Biocarbon}} + H_2O(l) + CO_2(g) + CO(g) + \underbrace{C_6H_{10}O_5\,(s)}_{\text{Levoglucosan (tar)}}$$

$$3C_6H_{10}O_5(s) \xrightarrow{\Delta} 8H_2O(g) + C_6H_8O(s) + 2CO(g) + 2CO_{2(g)} + CH_4(g) + H_2(g) + 7C(s)$$

$$2C_6H_8O(s) + 6H_2O(l) \rightarrow 14H_2(g) + 3CO_2(g) + 2CO(g) + 7C(s)$$

Impregnation of the biocarbon with H_3PO_4 and KOH produced modified biocarbons in a series of reactions (Ali *et al.,* 2014).

$$H_3PO_4(l) + HO - cellulose(s) \rightarrow Cellulose - O - PO_3H_2(s) + H_2O(l)$$

$$Cellulose - O - PO_3H_2(s) \xrightarrow{\Delta} PO - C(s) + H_2O(l) + H_2(g) + CO_2(g) + CO(g) + CH_4(g)$$

$$PO - C(s) \rightarrow C(s) + H_3PO_4(l)$$

$$C_nH_xO_y(s) + KOH(l) \xrightarrow{\Delta} (Cellulose - O - K)(s) + H_2O(l)$$

$$(Cellulose - O - K)(l) \xrightarrow{\Delta} C(s) + C + C - O - K(s) + tar(s) + Gases(g)$$

Physicochemical Characteristics: In order to access the appropriateness of the biocarbons obtained from Nipa palm leaves as adsorbent and to compare with commercial activated carbon (CAC), eight physicochemical properties were evaluated (Table 1). The carbon yield obtained for biocarbons were 33.7 ± 0.96% (PMB), 56 ± 0.19% (AMB) and 67.6 ± 0.21% (BMB) which were compared with CAC (98.53 ± 1.8). The results show that, the highest carbon yield (67.6 ± 0.21%) was recorded for base reagent activated biocarbon (BMB). CAC data was compared with Nipa

derived biocarbons and it revealed that BMB is of higher quality than AMB and PMB.

The relative loss of carbon during transportation, handling, and regeneration is related to mechanical strength, which can be measured by attrition level. The percent attrition obtained for the biocarbons and CAC are 64.26 ± 1.11, 42.11 ± 0.99, 82.2 ± 1.03 and 94.1 ± 1.09 for PMB, AMB, BMB and CAC respectively. The attrition of commercial granulated activated carbon (GAC) is in range of 70-90 % (Adowei *et al*., 2015).

From the data, the attrition levels of biocarbons produced from Nipa palm shows that BMB is harder than PMB and AMB respectively
.

Table 1: Physicochemical physiognomies of biocarbons and CAC

	Biocarbons			
	PMB	AMB	BMB	CAC
Carbon Yield (%)	33.7 ± 0.96	56 ± 0.19	67.6 ± 0.21	98.53 ± 1.8
Attrition (%)	64.26 ± 1.11	42.11 ± 0.99	82.2 ± 1.03	94.1 ± 1.09
pH	7.32 ± 0.44	6.41 ± 0.42	7.81 ± 0.47	7.21 ± 0.38
Ash content (%)	12.5 ± 1.09	10.2 ± 1.08	7.4 ± 1.05	17.2 ± 1.06
Moisture content (%)	12 ± 0.06	10 ± 0.03	11 ± 0.02	14 ± 0.08
Iodine number (mg/g)	334 ± 2.17	298 ± 1.96	224 ± 2.06	254 ± 2.11
Porosity (%)	75 ± 1.33	79 ± 1.21	65 ± 0.98	70 ± 1.22
Surface area m²/g	546 ± 0.45	488 ± 0.98	471 ± 1.02	522 ± 0.79

The acidity or basicity of activated carbon is dependent on several factors such as preparation, surface active oxygen groups and treatment method. The biocarbon derived from acidic reagent treatment was slightly lower in pH than those impregnated with KOH and H_2O. The acidity or basicity measured in terms of pH shows levels of 6.41 ± 0.11 to 7.81 ± 0.12 which is within the acceptable pH range (6 – 8) for activated carbons in most applications (Qureshi *et al.,* (2008). Relatively low biocarbon ash content is desirable because it is a sign of excellent mechanical strength. Biocarbons from Nipa palm leaves generated low percent ash which makes them comparable to CAC. The ash content for the Nipa palm biocarbons were 5.8 % (PMB), 4.3 % (AMB) and 3.7% (BMB) respectively.

The removal of volatile constituents in samples during thermo-degradation process can be measured by moisture content. Relatively low moisture content was observed for the biocarbons: PMB (6.5 %), AMB (6.4 %) and BMB (7.1 %) respectively. According to Aziza and co-workers (2008), the moisture content of CAC ranged between 2 – 5 %. Comparing CAC with Nipa palm biocarbons show that, PMB, AMB and BMB may serve as potential resources for adsorption process in a fixed bed column reactors. Development of internal porosity happens in thermo-degradation of carbon to create active surfaces. Measurement of the biocarbons porosity revealed that BMB had the highest porosity of 79 %, followed by PMB (73 %) and AMB (66 %).

Surface area of biocarbon is an important parameter to access the potential adsorption suitability of a precursor material. Specific surface area of the biocarbons are 488, 441 and 681 m²/g for PMB, AMB and BMB respectively. The data showed that BMB had the largest surface area, which is an essential criteria for improved adsorbent capacity and efficiency because surface area provides enormous pore volumes thereby increasing the

number of available active sites. The quantity of iodine adsorbed by one gram of biocarbon at equilibrium is a measure of the iodine number and the values for the biocarbons produced from Nipa palm leaves follow the order: BMB (814.5 mg/g) > PMB (622.8 mg/g) > AMB (431 mg/g). Higher iodine number indicates greater porosity, consequently, the data shows that BMB is a better adsorbent material with superior micropore content than the others.

Optimization of COD Reduction of Methyl Red in Water
Optimum process conditions such as biocarbon dosage, initial methyl red concentration, initial pH of methyl red solution, and refluxing time for digestion of methyl red were evaluated to assess their effects during COD reduction of methyl red in water by Nipa palm biocarbons and commercial activated carbons.

Effect of Biocarbon Dosage on COD Reduction
The measured quantity of an adsorbent used to contact aqueous solution has significant effect on the process of removal. Several investigations (Kapadia *et al.,* 2000, Tarawou *et al*., 2007) have revealed that, large dosage of biocarbon provides greater sorption sites, porosity and surface area thereby enhancing the attenuation capacity. The optimum dosage of biocarbons and CAC were evaluated by percent COD removal of methyl red in water (Figure 2). The result showed that, percent COD reduction by PMB, AMB, BMB and CAC increased with increase in biocarbon dosage with maximum dosage obtained around 0.8 g/50ml, which translates to 93.1% (PMB), 93.7% (AMB), 95.1% (BMB) and 96.6 % (CAC) respectively at 30°C. Comparative analysis of COD reduction between Nipa biocarbons and CAC showed that, BMB gave optimum COD reduction for methyl red in water.
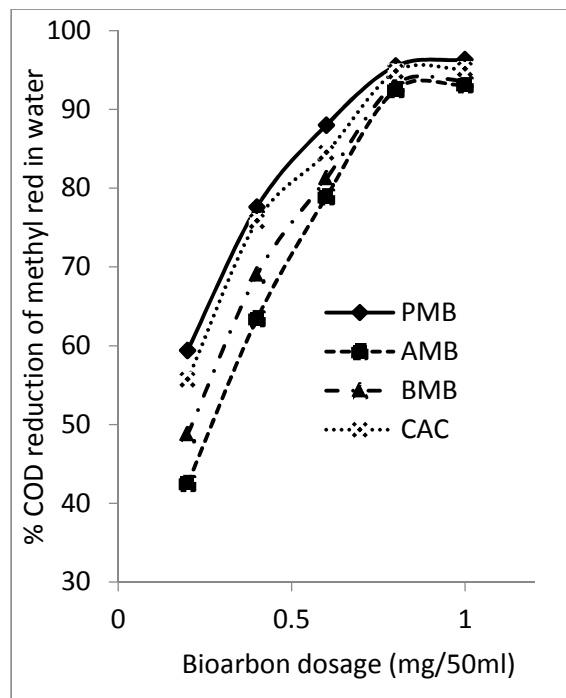
Fig 2: Effect of biocarbon dosage on COD reduction of methyl red in water

Effect of Initial Methyl Red Concentration on COD Reduction: The relationship between percent COD reduction and initial methyl red concentrations for the biocarbons and commercial activated carbon are presented in Figure 3. Optimal COD reduction for methyl red in water by PMB, AMB, BMB and CAC were 82.7%, 76.7 %, 83.5 %, and 83.3 % respectively. The data showed that percent COD reduction increased from lower concentration of 20 mg/l to a maximum around 40 mg/l and gradually decreased for the remaining monitoring concentrations. At lower concentrations, significant amount of methyl red was attenuated from solution since the medium could interact with the binding sites on the surface of the biocarbons to yield higher percent reduction. At higher concentrations of methyl red in water, lower attenuation were observed because surface saturation on the biocarbons occur quickly and there were no further take up of methyl red, hence, the amount reduced become smaller as initial concentration increased

Effect of pH on COD Reduction: Methyl red is an anionic azo dye (Ashraf et al., 2006), which turns red to yellow within pH range of 4.4 to 6.2. pH of dye solutions play significant role in tinting of textile and paper materials. During dyeing process, anions are favorably attached to materials at lower pH values due to availability of H^+ ions, while at high pH values, cations are attracted to the materials because of the

presence of negatively charged surface sites on materials. The effect of pH can be explained by surface charges on the attracting material. Hence, the reduction of methyl red in water as a function of pH was also investigated.

The percent COD reduction of methyl red by the biocarbons and CAC as presented in Figure 4 showed that COD reduction strength rises as pH value increased from 2 to 9 reaching optimal value at pH 5. It was observed that, poor COD reduction of methyl red occurred at the two extremes of the pH levels. Excellent methyl red degradation was achieved at pH range 4 – 6.
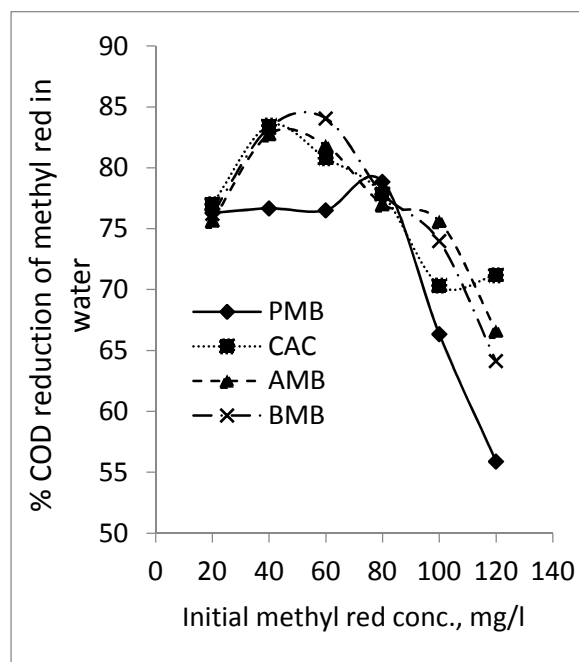

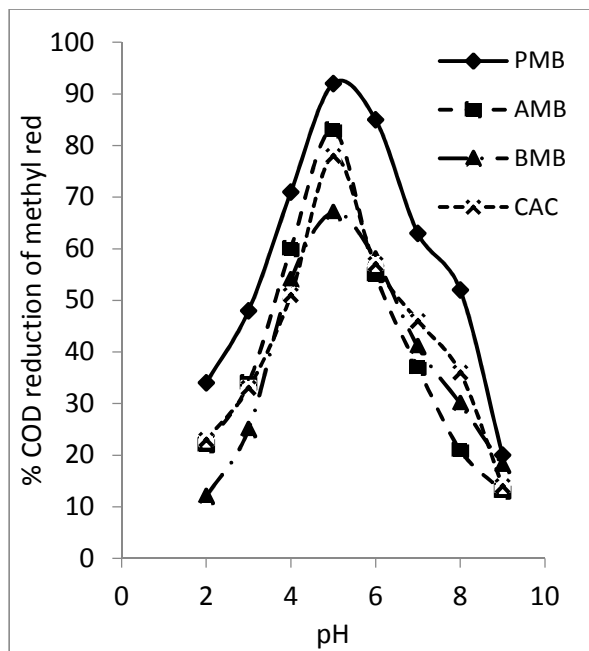**Fig 3**: Effect of initial methyl red concentration on COD attenuation

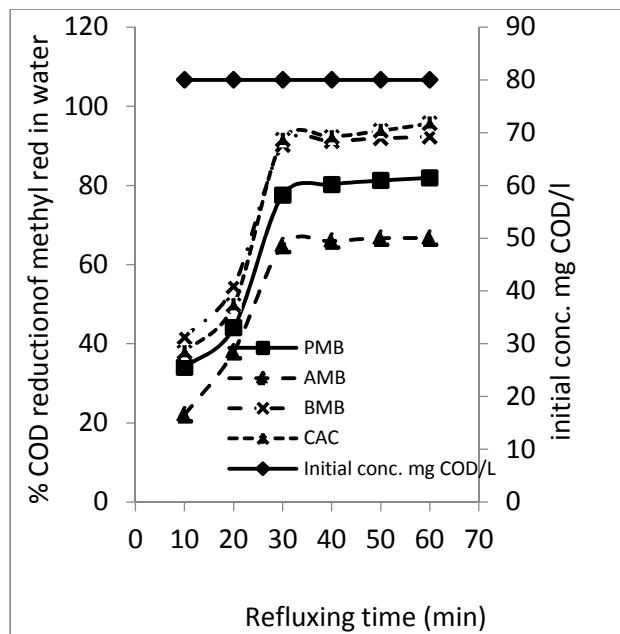**Fig 4**: Effect of pH on COD reduction of methyl red in water

Fig 5: Effect of refluxing time on COD reduction of methyl red in water

Effect of Refluxing Time on COD Reduction: The refluxing time is essential in the consideration of the optimum COD reduction of organic contaminant and may be adopted in providing optimum degradation time. The consequence of refluxing time on COD reduction at fixed methyl red initial concentration (100 mg/l) and fixed refluxing temperature (150°C) by the biocarbons and CAC are shown in Figure 5. The data indicates that degradation time is not dependent on biocarbon type; and maximum COD reduction could be achieved within 30 min of refluxing. The equilibrium time indicate the completeness of degradation of organic components. The rapid degradation time indicates that easy-to-digest samples may be studied with confidence in short period of time.

Equilibrium Models Treatment of Experimental Data
Equilibrium models are essential conditions in the design of adsorption systems because they provide baseline data for possible scale-up operation. Equilibrium COD reduction of methyl red in water by biocarbons and CAC were estimated by Langmuir and Freundlich equilibrium models

Langmuir Isotherm: Langmuir isotherm has a hypothetical basis and assumed that a surface contains a specified quantity of equal sites where certain class of molecules can stick physically or chemically. In order to ease the approximation of the COD reduction capacity, the experimental data of methyl red in by biocarbon and CAC were applied to the Langmuir isotherm equation by plotting ($\frac{C_e}{q_e}$) against C_e (Figure 6). The computed COD reduction capacities (q_{max}, mg/g), Langmuir constants (K_L, dm^3/g), and coefficient of determinations (R^2) for methyl red removal in water are presented Table 2. The maximum COD reduction (q_{max}) capacities obtained were 2.15 mg/g (PMB), 8.73 mg/g (AMB), 11.83 mg/g (BMB) and 62.60 mg/g for CAC respectively. Amongst the Nipa palm biocarbons, the Langmuir maximum COD reduction COD reduction capacity of BMB for methyl red is higher than PMB and AMB but relatively lower CAC. The Langmuir coefficient for PMB (8.70 x 10^{-1} dm^3/g) to attenuate methyl red in water was greater than that of AMB and BMB, indicative of requiring higher energy for action. Comparing the Langmuir constant coefficients values for Nipa palm biocarbons and CAC demonstrations that BMB is a better biocarbon option than PMB and AMB
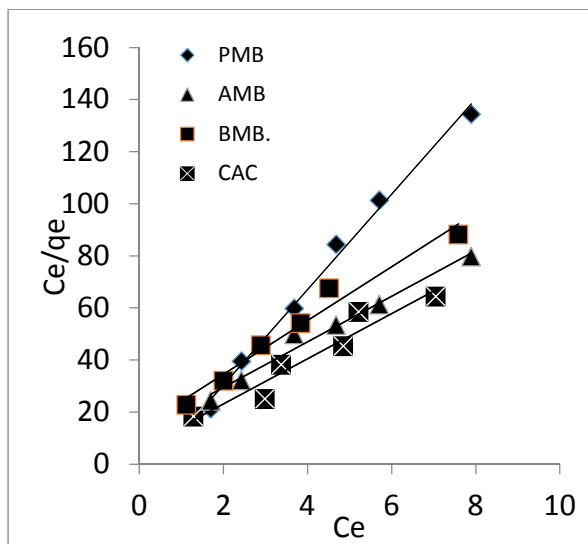
Fig 6: Langmuir equilibrium isotherm model of COD reduction of methyl red in water

Freundlich Isotherm

Freundlich isotherm model provides experimental equation for testing non-perfect materials that have heterogeneous surfaces for attraction. The model is adopted to approximate data for physical adsorption systems especially in liquids and was used to approximate COD reduction strength (figure 7) of methyl red in water by PMB, AMB, BMB and CAC. The Freundlich constant, K_F, an equilibrium partition coefficient associated with bonding energy provided the degree of COD reduction. In practice, large K_F value is a pointer to enhanced contaminant reduction. The K_F values obtained for COD reduction of methyl red in water by different biocarbons and CAC were 0.207 (PMB), 0.570 (AMB), 0.447 (BMB) and 0.783 (CAC) respectively.

Table 2 Langmuir maximum COD reduction (q_{max}) capacity (mg/g) for methyl red in water

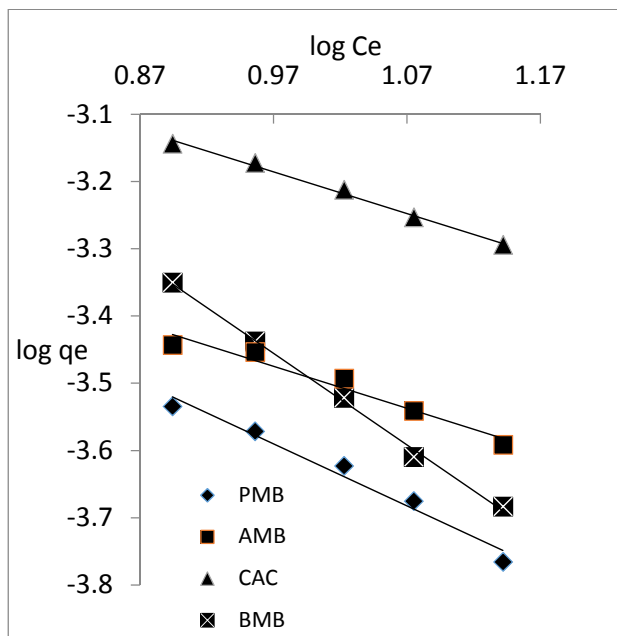|	Langmuir isotherm Parameters			Freundlich Isotherm Parameters		
	q_{max} (*mg/g*)	(K_L, dm^3/g)	R^2	K_F	n	R^2
PMB	2.15	8.70×10^{-1}	0.945	0.207	0.357	0. 899
AMB	8.73	9.49×10^{-1}	0.875	0.570	0.1605	0.898
BMB	11.83	7.0×10^{-1}	0.981	0.447	0.6209	0.906
CAC	62.60	2.0×10^{-1}	0.994	0.783	0.8765	0.927

Fig 7: Freundlich equilibrium isotherm model of COD reduction of methyl red in water

COD Attenuation Favourability: The favourability or unfavourability of reducing COD in water contaminated by methyl red was assessed using the Langmuir isotherm coefficient (K_L) and Freundlich isotherm model parameter (1/n). To predict the favourable or unfavourable by K_L, the dimensionless separation index (S_i) proposed by Poots and co-workers (1978) was applied. In its application, reduction favourability or unfavourability may be assessed based on the value of S_i obtained from computation. In so doing, if computed value of $S_i > 1$, COD reduction is unfavourable and if $0 < S_i < 1$, COD reduction is favourable. In the case of Freundlich 1/n parameter; a favourable COD reduction corresponds to a value of $0 < 1/n < 1$ while unfavourability tallies with $1/n > 1$. Computational data reveal values of $S_i < 1$ and $1/n < 1$, therefore COD reduction of methyl red in water using Nipa biocarbon

is favourable and the technique may be adopted as a practicable option for removing low molecular weight organic contaminants in aqueous system.

Kinetic Model Treatment of Experimental Data: In water and wastewater treatment systems, kinetic models can be used to predict the rate of reactions for designing appropriate treatment plants, such studies may provide insight into the reaction pathways and mechanisms. Kinetic models extensively used in this regards are Langergren pseudo-first order kinetic model (Gupta *et al*., 1994; Gaid *et al* 1994, Horsfall *et al*., 2005) and pseudo-second order kinetic model (Ho *et al*., 1995, 1998 and Horsfall and Spiff, 2005. In this paper, these two models were adopted to judge the reflux time experimental data from COD reduction of methyl red in water, whose parameters are presented in Table 3.

Table 3: COD reduction parameters from pseudo-first and - second order rate models

Carbons	Pseudo-first order equation parameters				Pseudo-second order equation parameters			
	PMB	AMB	BMB	CAC	PMB	AMB	BMB	CAC
q_e, mg/g	5.32	2.10	6.10	7.90	6.41	2.80	8.77	9.48
r^2	0.85	0.416	0.822	0.854	0.997	0.995	0.999	0.997
k_1 and k_2 x 10^{-3}	4.38	1.15	9.66	4.38	9.19	6.0	3.02	2.24
h_o					0.357	0.411	0.641	0.809

q_e = COD reduction capacity at equilibrium, (mg g^{-1}),
r^2 = Coefficient of determinations
k_1 = Pseudo-first order rate constant, (min^{-1})
k_2 = Pseudo-second order rate constant, (mg g^{-1} min^{-1})
h_o = Ho's constant related to initial COD reduction rate, (mg g^{-1} min^{-1})

Langergren Pseudo – First Order Kinetics
Langergren (1998) pseudo-first order kinetic model was used to evaluate the rate constants (Fig 8). The data showed that the rate constants (k_1, min^{-1}) for COD reduction of methyl red in water are 4.38 x 10^{-3}, 1.15 x 10^{-3}, 9.66 x 10^{-3} and 4.38 x 10^{-3} for PMB, AMB, BMB and CAC respectively. The pseudo-first order rate constants, k_1, for BMB was higher than PMB and AMB. The values for coefficient of determinations, R^2, from the Langergren pseudo-first order kinetic plot are 0.854, 0.416, 0.822 0.854 for PMB, AMB, BMB and CAC. The plots are non-linear, indicating that pseudo-first order kinetic is unsuitable to describe the COD reduction process of methyl red in water by the biocarbons and CAC.
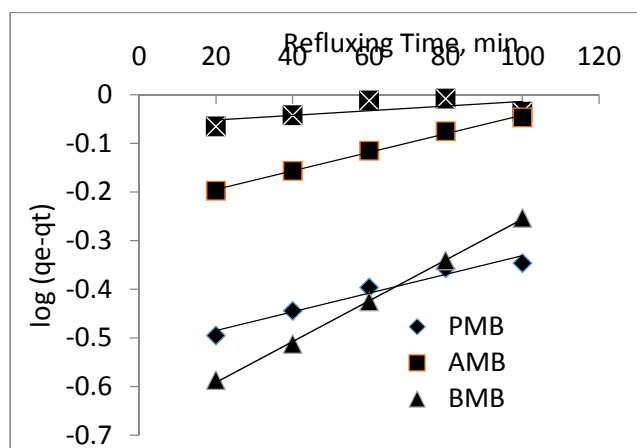

Fig 8. Lagergren COD reduction plots for methyl red in water

Pseudo – Second order Kinetics: Since the expected curvature did not fit the experimentally derived data for the pseudo-first order kinetic model; a pseudo-second order rate equation (Ho *et al.,* 1995) was applied by plots of $\frac{t}{q_t}$ against *t* (Figure 9). The equilibrium COD reduction capacities (mg/g) obtained from the graph for biocarbons and CAC were 13.94 (PMB), 2.80 (AMB), 51.77 (BMB) and 53.48 (CAC); respectively. The behaviour indicates that PMB has the lowest COD reduction capacity. The rate constants (k_2, g/mg .min) were 9.19 x 10^{-3} (PMB), 26.0 x 10^{-3} (AMB), 0.302 x 10^{-3} (BMB) and 0.224 x 10^{-3} (CAC) respectively. The R^2 values for COD reduction by the biocarbons and CAC are >> 0.995, indicating that the pseudo-second order rate law is very good in describing the COD reduction behaviour of the biocarbons.
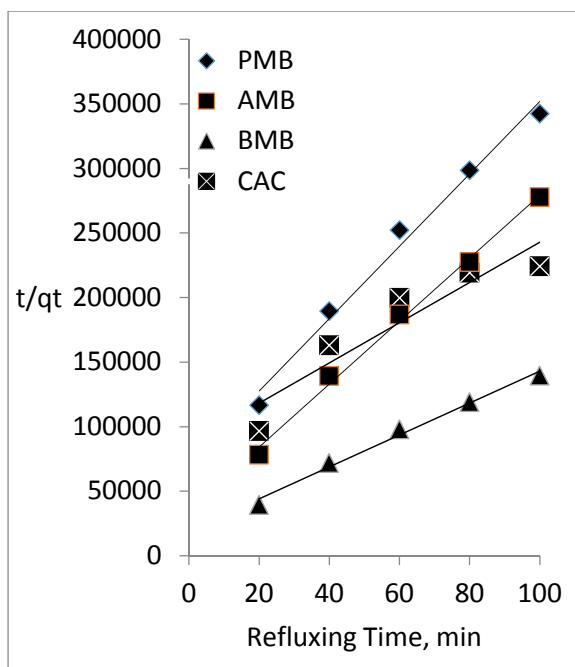

Fig 9: Pseudo-second order COD reduction plots for methyl red in water

Thermodynamic Model Treatment of Experimental Data

Spontaneity of COD reduction process of methyl red in water was assessed by computing the apparent Gibbs free energy (ΔG^o) using Langmuir isotherm model equilibrium constant (K_L). By this assessment, a process is spontaneous at a given temperature, if ΔG^o is a negative quantity with values up to – 20 kJ/mol and non-spontaneous if ΔG^o is a positive quantity. The apparent Gibbs free energy of COD reduction for methyl red in water by biocarbons and CAC as computed are presented in Table 4. The values of ΔG^o (kJ/mol) computed for PMB, AMB, BMB and CAC are -3.51, - 0.13, - 5.90 and - 4.06 respectively. The negative values of ΔG^o indicate that COD reduction of methyl red in water using biocarbons and CAC are spontaneous in nature requiring negligible amount of energy. Since the values of ΔG^o obtained were < – 20 kJ/mol, it means that the interactions between methyl red and biocarbons are electrostatic and the prime mechanism is physisorption.

Table 4: Computation of ΔG^o, (kJ/mol) of COD attenuation of methyl red in water

Carbons	PMB	AMB	BMB	CAC
	-3. 51	-1. 31	- 5.90	-4.06

Statistical Evaluation of COD Reduction Capacity Studies: The reliability of the analytical data were assessed by one-way ANOVA in order to measure the uncertainties associated with computed results. In so doing a null hypothesis to compare the COD reduction potential of biocarbons (PMB, AMB and BMB) to reduce methyl red in water at 0.05 significant level was made. The result shows that, F_{exp} (0.74) < F_{crit} (4.07) implying that there is no difference in the potential capacities of the biocarbons to attenuate methyl red in water at the 0.05 significant level. The p-value obtained from computation (Table 5) is compared with the significance level (0.05). Because the p-value (0.5582) > significant level (0.05), there is no significant differences in COD reduction capacity among the biocarbons obtained from Nipa palm leaves.

Table 5 One–Way Analysis of Variance (ANOVA) at α = 0.05 to compare the Nipa palm biocarbons and CAC

Sources 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

Conclusions: In conclusion, the series of COD reduction experiments and evaluation of the data by various equilibrium and kinetic models revealed that Nipa palm biocarbons are capable of reducing organic contaminants in aqueous media especially at dilute concentrations. Successive government has developed various programmes in the Niger Delta region to exterminate the Nipa palm plant due to its invading capacity; however, this investigation has revealed that apart from tapping natural resources such as sugar, alcohol, paper and food stuff from the Nipa palm, its waste could be useful as an industrial source for production of biocarbons for various uses.

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