

Adsorption of Selected Synthetic Organic Compounds in Aqueous Solutions Using Carbonized and Surface-Modified Carbons from Fresh Nipa Palm *Nypa Fruticans Wurmb* Fronds

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Abstract

Synthetic Organic Chemicals (SOCs) are man-made carbon-based compounds that are less likely to escape into the atmosphere and hence could get into aquatic water bodies through terrestrial runoff or discharge from factories. This paper therefore investigated the adsorption of certain SOC 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. The microstructure of the Nipa palm biomass and carbonized carbon evaluated by scanning electron microscopy (SEM); energy dispersive x-ray (EDX) and FTIR has already been published elsewhere. 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. Kinetic assessment of the results showed that, pseudo-first order kinetic equation did not provide a very good description of COD reduction of the SOC in aqueous solution by the Nipa palm derived carbons. Thermodynamic assessment by Gibbs free energy (ΔG_0 , KJ/mol) revealed that ΔG_0 values were negative (1.45 - 5.89). 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 chemicals; Chemical oxygen demand; Adsorption; Nipa Palm; Carbonized carbon; Wastewater

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. These compounds have adverse health effects. Also their presence in water may reduce dissolved oxygen concentrations, which is detrimental to aquatic life [1]. Therefore, treatment of wastewater is necessary to correct its characteristics in such 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. However, Adsorption is the most successful of these methods due to its simplicity and low cost. Chemical oxygen demand (COD) 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 [2]. Chemical Oxygen Demand (COD) is a major parameters used as routine surrogate tests for measuring the load of organic carbon into the environment. Also, COD is a cheap method for the determination of organic load in waste water. The objective of this paper, therefore, is to investigate the feasibility of removing selected synthetic organic compounds in aqueous solutions using physically (distil H_2O) carbonized, acidic (3.27 M, H_3PO_4) 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.

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. 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 [3]. 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 ($FeSO_4 \cdot 7H_2O$), 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 (AquaNucha).

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Instrumentation: The instrument used were 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 [4,5].

Carbonization of Biomass: The dried Nipa palm biomass from the fronds wer carbonized by taking about 25 ± 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. 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. The solids were then sun dried, followed by oven drying at 100 °C for one hour and then weighed. The dried sample was sieved through a 106- μ m mesh Tyler sieve and the fractions < 106 μ 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 [6].

Activation of Biomass: The activated carbons were prepared by a one-step pyrolysis method. 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 [7]. The pyrolyzed carbons were washed, using 10% HCl to remove surface ash, followed by rinsing with distilled water to remove residual acid 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 μ m mesh Tyler sieve. Fractions < 106 μ m were collected and kept in an air-tight container for use. Washing was complete when a pH of 7 ± 0.5 was ascertained.

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 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 μ m mesh Tyler sieve. Fractions < 150- μ m were collected and kept in an air-tight container for use. Washing was complete when a pH of 7 ± 0.5 was ascertained [8].

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

Carbons	Raw SOC solution	DMABA	
		Treated SOC solution	% COD reduction
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			
Carbons	Raw SOC solution	Treated SOC solution	% COD reduction
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			
Carbons	Raw SOC solution	Treated SOC solution	% COD reduction
	22.44	1.054	95.303
PCC	22.44	1.387	93.81
AAC	22.44	1.198	94.66
BAC	22.44	1.054	95.30
CAC			

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).

Result

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 mgL⁻¹ to 1.96 mgL⁻¹ (PCC), 1.65 mgL⁻¹ (AAC), 1.47 mgL⁻¹ (BAC), 1.11 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 mg L⁻¹. The reduction in COD was from 67.42 mgL⁻¹ to 3.12 mgL⁻¹ for PCC with 95.37 % removal efficiency, 67.42 mg L⁻¹ to 2.61 mg L⁻¹ for AAC with a removal efficiency of 96.13 %, 67.42 mg L⁻¹ to 2.24 mgL⁻¹ for BAC with 96.67 % removal efficiency and 67.42 mgL⁻¹ to 1.84 mgL⁻¹ 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⁻¹. 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⁻¹ to 1.05 mgL⁻¹ (PCC), 1.39 mgL⁻¹ (AAC), 1.20 mgL⁻¹ (BAC), 1.05 mgL⁻¹ (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 Healy et al. (2006) 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/m²/d gave a filter COD, TSS and total TKN loading rate of 14, 3.7 and 2.1 g/m²/d, respectively and produced consistent COD and TSS removals of greater than 99 % and an effluent NO₃-N concentration of 42 mg L⁻¹ (accounting for an

86 % reduction in total nitrogen (Tot-N).

Acknowledgment

None

Conflict of Interest

None

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