

Elimination of Chemical Oxygen Demand in Aqueous Solutions Contaminated with 2 - (N, N - Dimethyl - 4 - aminophenyl) - azo - benzene Carboxylic Acid (DMABA), N - propanol and Kerosene: Effect of pH

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Abstract: *The pH of the contact solution is an important parameter controlling the adsorption process in terms of acidity. The adsorption capacity decreases as the acidity of the contact solution increases. 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 effect of pH on the elimination of 2 - (N, N - Dimethyl - 4 - aminophenyl) - azo - benzene carboxylic acid (DMABA), n - propanol and kerosene in contaminated aqueous solutions by physically activated Carbon (PCC), acidic reagent activated carbon (AAC), basic reagent activated carbon (BAC) obtained from Nipa palm ferns and commercial activated carbon (CAC) as a control. The index of measurement used was chemical oxygen demand. The pH - dependency on the COD reduction were 66.7 %, 58.2 %, 76.8 % and 89.4 % for PCC, AAC, BAC and CAC respectively. The data showed that with or without activation of the carbons, the COD elimination improved as pH value raised from 2 to 9.2. An optimum in the COD elimination was obtained at about pH 8.5. The results obtained show that pH has a profound effect on the elimination process, this is because increase in pH of the contact solution leads to decrease in elimination capacity, thus a disruption in the elimination of organic chemicals in contaminated aqueous system, hence, selection of optimum pH is very essential.*

Keywords: Synthetic organic chemicals; chemical oxygen demand; adsorption; Nipa Palm; pH

1. Introduction

2 - (N, N - dimethyl - 4 - aminophenyl) azobenzenecarboxylic acid (DMABA) is methyl red, also called C. I. Acid Red 2, is an indicator dye that turns red in acidic solutions. It is an azo dye, and is a dark red crystalline powder. N - propanol (also known as 1 - propanol, n - propanol alcohol, propan - 1 - ol, propyl alcohol) is a primary alcohol in which the OH entity is bonded to a primary carbon atom. N - propanol is used in the coatings industry, n - Propanol is used as a semi - volatile alcohol for improving the drying properties, for example in the manufacture of alkyd resin paints, baking finishes and electrodeposition paints. In the cleaning agent sector, it is added to floor polishes and metal degreasing agents. Kerosene is typically pale yellow or colourless and has a not - unpleasant characteristic odour. It is obtained from petroleum and is used for burning in kerosene lamps and domestic heaters or furnaces, as a fuel or fuel component for jet engines, and as a solvent for greases and insecticides. DMABA, N - propanol and Kerosene are potential man - made chemicals and could be ascribed as synthetic organic chemicals.

Mainly, SOCs are carbon - based compounds of man - made origin that can get into water through runoff from croplands and or discharge from industries. SOCs may also come from urban storm water runoff and septic systems. Hence, they originate from domestic, commercial and industrial activities. SOCs are used as pesticides, defoliant, fuel additives and as ingredients for other organic compounds. Some of the more

well - known SOCs are Atrazine, 2, 4 - D, Dioxin and Polychlorinated Biphenyls (PCBs). Some common and not well - known amongst the SOCs include primary alcohols, lower petroleum fractions and organic dyes. Many of these compounds have been identified in wastewater and water supplies [1, 2, and 3]. These compounds have adverse health effects. Also, their presence in water may reduce dissolved oxygen concentrations, which is detrimental to aquatic life [4, 5].

Therefore, treatment of wastewater is necessary to correct its characteristics in such 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 [6 - 10]. However, Adsorption is the most successful of these methods due to its simplicity and low cost [11 and 12].

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. Chemical Oxygen Demand (COD) is a major parameter used as routine surrogate tests for measuring the load of organic contaminant in aqueous system [13], this is because COD method is cost -

effective, simple and accurate for the determination of organic load in waste water [14].

However, the objective of this paper, therefore, is to investigate the effect of pH on the elimination of This paper therefore investigated the effect of pH on the elimination of 2 - (N, N - Dimethyl - 4 - aminophenyl) - azo - benzene carboxylic acid (DMABA), n - propanol and kerosene in contaminated aqueous solutions by physically activated Carbon (PCC), acidic reagent activated carbon (AAC), basic reagent activated carbon (BAC) obtained from Nipa palm ferns and commercial activated carbon (CAC) as a control

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 [15 - 16].

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. The 106 µm mesh Tyler sieve used in this research work was obtained from the Geology laboratory of the University of Port Harcourt [15 - 16].

Chemicals: The ferrous ammonium sulphate, ferroin indicator, iron sulphate (FeSO₄.7H₂O), hydrogen peroxide H₂O₂ (30 % W/V), H₂SO₄, sodium hydroxide NaOH, acetic acid (CH₃COOH), potassium dichromate (K₂Cr₂O₇), mercuric sulphate HgSO₄, silver sulphate Ag₂SO₄, manganese oxide, 10 % HCl, potassium hydroxide 10 % KOH (0.9 M), 10 % (3.27 M) H₃PO₄, 2 - (N, N - Dimethyl - 4 - aminophenyl) - azo - benzene carboxylic acid (DMABA) (ii) kerosene and (iii) n - propanol and commercial activated carbon (AquaNucha).

Activation of Biomass: Three activated carbons and a commercial carbon were prepared. They are (i) Commercial Activated Carbon (CAC) (ii) Physically activated Carbon (PCC), (iii) Acidic reagent activated carbon (AAC) and (iv) Basic reagent activated carbon (BAC). The methodology has been carefully and exhaustively presented in previous works [15 - 16].

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.

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) 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 (Gimba *et al.*, 2004; Adowei *et al.*, 2016). 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 (Fan *et al.*, 2003). The solids were then sun dried, followed by oven drying at 100 °C for one hour (Itodo *et al.*, 2009) 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 [15 - 16].

Activation of Biomass: The activated carbons were prepared by a one - step pyrolysis method (Ash *et al.*, 2006; Sugumaran and Seshadri, 2009). The activated carbons produced were called (i) Acidic reagent activated carbon (AAC) and (ii) Basic reagent activated carbon (BAC)

(i) **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) H₃PO₄ 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 (Fan *et al.*, 2003; Adowei *et al.*, 2016) 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 (Ahmedna *et al.*, 2000; Adowei *et al.*, 2016) [15 - 16].

(ii) **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 (Fan *et al.*, 2003; Adowei *et al.*, 2016) 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 [15 - 16].

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 [15 - 16]. .

(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 [15 - 16]. .

Also a mass weight can be used to prepared 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 3.1

$$\text{Density, g/ml} = \frac{\text{mass (g)}}{\text{volume (ml)}} \dots \dots \dots 3.1$$

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 [15 - 16]. .

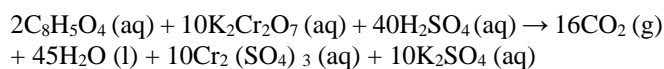
Determination of Effect of initial pH at 30°C

2.0 g each of PCC, AAC, BAC 106 µm mesh particle size and CAC were weighed and introduced into several 250 ml conical flasks. 50 ml of 100 mgL⁻¹ DMABA, kerosene and n - propanol solution were added to the flasks. 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 a solution of either conc. HCl or NaOH. The mixtures were transferred to 150 ml plastic sample containers and shaken for 60 min at 150 rpm. At the end of 60min, the suspensions were allowed to stand on the bench for 30 min to separate and then filtered using Whatman No 40 filter paper. The clear supernatant SOC solutions were analyzed for final COD (COD_f).

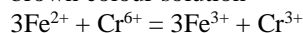
Determination of Chemical Oxygen Demand (COD)

COD measurement is a two - step process [2, 17]: Digestion and Determination. The chemistry of these two processes is explained below.

Digestion Step: organic matter is oxidized by dichromate ions in sulphuric acid to CO₂ and H₂O. During heating the dichromate ions (Cr₂O₇⁻²) form orange - colored solutions.



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



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

Analysis of Experimental Data

Calculation of COD from Experimentation: The COD values of the respective solutions and blank were estimated as presented in eqn 1.

$$\text{COD as mg O}_2/\text{L} = \frac{(A-B) \times M \times 8000}{V_s} \dots (1)$$

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

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

$$\% \text{ COD Removed} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \times 100 \dots \dots \dots (2)$$

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).

Analytical Precision and Quality Control

Care was taken during sample collection and preservation. Glassware was properly cleaned and reagents were of analytical grade. Reagent blanks, method blanks and working standards/solutions were prepared freshly. For quality control purpose a commercial activated carbon (CAC) with the trade name *Aqua Nucha* was purchased and used as a control. *Aqua Nucha* was supplied by Rovet Scientific Ltd, Benin City.

Statistical Analysis of Experimental Data

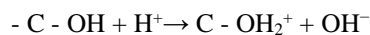
The reliability of experimental results was obtained by carrying out triplicate analysis and calculation of the mean, standard deviations, standard errors and analysis of variance (ANOVA).

3. Results and Discussion

Effect of pH on COD Reduction

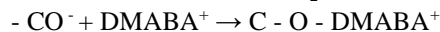
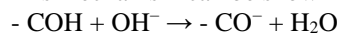
DMABA is a dye and the pH of the dye solutions plays important role in the whole adsorption process and particularly on the adsorption capacity, influencing not only the surface charge of the adsorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry. It is a commonly known fact that the anions are favorably adsorbed by the adsorbent at lower pH values due to presence of H^+ ions. At high pH values, cations are adsorbed due to the negatively charged surface sites of activated carbons. Any oxide surface creates a charge (positive or negative) on its surface. This charge is proportional to the pH of the solution which surrounds the oxide particles ([18]. A convenient index of the tendency of a surface to become either positively or negatively charged as a function of pH is the value of the pH required to give zero net surface charge [19]. DMABA is cationic basic dye as denoted by the presence of the positive nitrogen ions in its structure; therefore, it is prone to electro - statically attract cations. The effect of pH can be explained considering the surface charge on the adsorbent material. At low pH values ($\text{pH} < 2$), the low adsorption observation was explained due to increase in positive charge (protons) density on the surface sites and thus, electrostatic repulsion occurred between the DMABA^+

molecules and the edge groups with positive charge ($\text{C} - \text{OH}_2^+$) on the surface as follows:



At higher ($\text{pH} > 2$), the surface of carbons becomes negatively charged and electrostatic repulsion decreases with increasing pH due to reduction of positive charge density on the sorption edges thus resulting in an increase SOC's adsorption.

This mechanism can be shown as follows:



A similar theory was proposed by several earlier workers for organic contaminant adsorption on different adsorbents [20, 21 and 22].

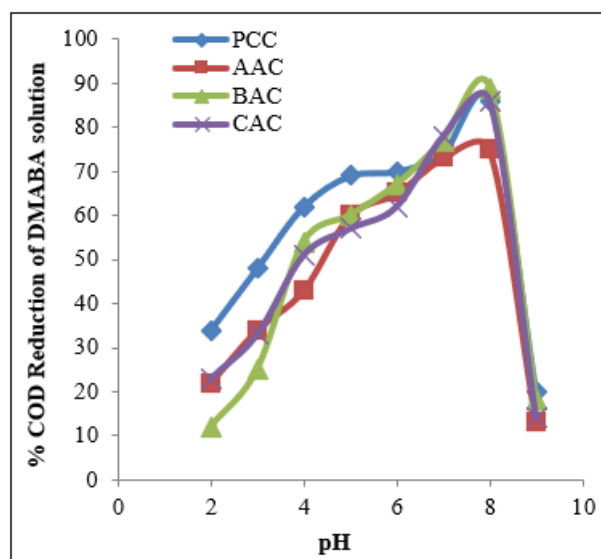


Figure 1: Effect of pH on COD reduction of DMABA solution by PCC, AAC, BAC and CAC at 30°C

The percent COD reduction of DMABA by PCC, AAC and BAC compared with CAC as presented in Figure 1 showed that COD reduction increased with an increase in pH from 2 to 10, with optimum conditions reached at pH 8. Only relatively poor elimination of DMABA was achieved under acidic conditions. This observation may be related to the presence of excess H_3O^+ ions competing with the protonated dye in aqueous solution for adsorption.

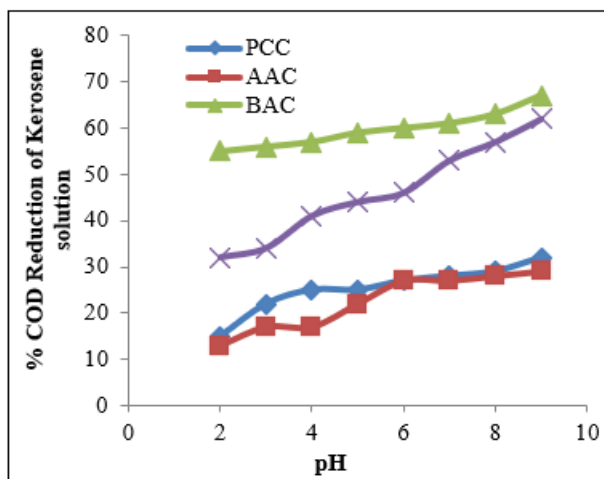


Figure 2: Effect of pH on COD reduction of kerosene solution by PCC, AAC, BAC and CAC at 30 °C

In order to study the effect of pH on COD reduction of kerosene solutions by PCC, AAC, BAC and CAC, experiments were carried out at 250 mg/L initial kerosene concentration with 100 mg/100 ml adsorbent mass at room temperature of $29 \pm 1^\circ\text{C}$ for 3 h equilibrium time. Results are presented in Figure 2. In the case of PCC, maximum COD reduction of 32.8% was recorded at pH 9. Between pH range of 2 - 6, the percentage of kerosene contaminant removal was nearly equal, $\sim 29\%$. Even though the data showed that, BAC adsorption efficiency is higher than that of PCC and AAC, no significant increase in kerosene removal efficiency was observed between pH ranges of 3 – 9 investigated.

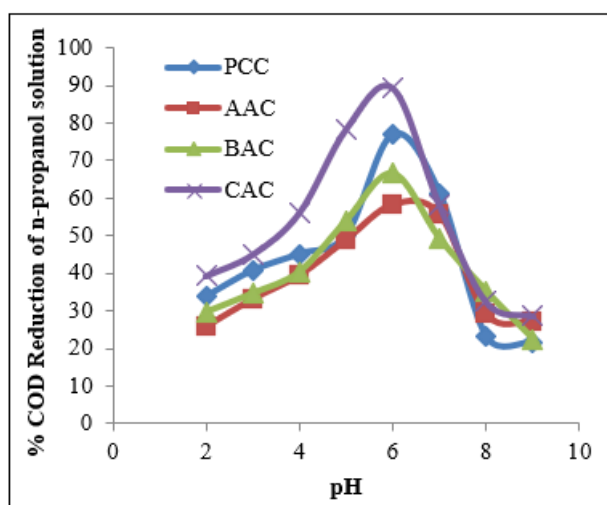


Figure 3: Effect of pH on COD reduction of n - propanol solution by PCC, AAC, BAC and CAC at 30 °C

The pH - dependency on the COD reduction of n - propanol solution with PCC, AAC, BAC and CAC at initial concentration of 100 mg/l was studied and is shown in 3. The data showed that with or without chemical activation of the carbons, the COD reduction increased as pH increased from 2 to 6.5, with maximum pH obtained between 5.5 and 7.0. This increase in pH resulted in the COD reduction of n - propanol solution by 66.7 %, 58.2 %, 76.8 % and 89.4 % for PCC, AAC, BAC and CAC respectively.

4. Conclusions

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 at optimum pH of 8.5. Production of carbons from the leaves of Nipa palm is feasible, economical and environment friendly. These removal potentials are significantly comparable to the commercial activated used to validate the carbons. The feasibility was further assessed by using separation factor; and the data obtained revealed that the interaction between the Nipa palm derived carbons and the various SOCs investigated are favourable and the predominant mechanism is physisorption. The outcome of this investigation has revealed that carbons developed from Nipa palm leaves are an attractive option for organic contaminants removal from aqueous solution.

Acknowledgement

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Abbreviations

AAC = Acidic reagent activated carbon
 ANOVA = analysis of variance
 BAC = Basic reagent activated carbon
 CAC = Commercial Activated Carbon
 COD = chemical oxygen demand
 DMABA = 2 - (N, N - Dimethyl - 4 - aminophenyl) - azo - benzene carboxylic acid
 FAS = ferrous ammonium sulphate
 PCC = physically activated Carbon
 SOCs = Synthetic Organic Chemicals

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