ELIMINATION OF CHEMICAL OXYGEN DEMAND IN AQUEOUS SOLUTIONS BY NIPA PALM LEAVES

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Abstract. The dosage of adsorbent has a significant consequence on the adsorption process. This short communication evaluates the effect of carbon dosage on the removal of chemical oxygen demand (COD) from organic substances contaminated aqueous solutions using Nipa palm leaves powder. The Nipa palm leaves powder were modified by distilled water (PCC), 10 % (3.27 M) H_3PO_4 (AAC), 10% KOH (BAC) solutions with Commercial Activated Carbon (CAC) used as the control. The result showed that, percent COD reduction by PCC, AAC, BAC and the CAC increased with increase in carbon dosage with maximum carbon dosage obtained around 0.8g/50ml. This optimum amount of 0.8g is capable of reducing COD level by 93.1%, 93.7%, 95.1%, and 96.6%, of DMABA by PCC, AAC, BAC and CAC at 30°C respectively. Meanwhile, the result for kerosene showed that COD reduction due to carbon dosage ranged from 25.5%-64.6%, 19.8%-55.8%, 20.5%-58.7% and 22.5%-61.4% by PCC, AAC, BAC and CAC respectively. The maximum COD reduction observed for kerosene was less than 65% and the percent COD reduction for n-propanol increased from 11.5 to 64.7% for PCC, 9.3 to 62.5% for AAC, 17.5 to 72.2% for BAC and 12.2 to 74.5% for CAC. Comparative analysis of the COD reduction as a function of the carbons produced from Nipa palm and CAC showed that, BAC gave optimum removal of DMABA, kerosene and n-propanol. 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 (Pereware et al., 2020; Adowei and Abia, 2016; Adowei et al., 2015). These compounds have adverse health effects. Also, their presence in water may reduce dissolved oxygen concentrations, which is detrimental to aquatic life (Adowei and Abia, 2016; Abia et al., 2003). 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 (Verla et al., 2014; Ekpete et al., 2012; Jnr and Spiff, 2005; Horsfall et al., 2004; Horsfall Jr and Abia, 2003). However, Adsorption is the most successful of these methods due to its simplicity and low cost (Abechi et al., 2013; Adinata et al., 2007). 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 carbon into the environment (Fadini et al., 2004). Also, COD is a cheap method for the determination of organic load in waste water (Ademiluyi and Braide, 2012). The objective of this paper, therefore, is to investigate the feasibility of removing chemical oxygen demand (COD) in organic substances contaminated solutions using physically (distil H2O) carbonized, acidic (3.27 M, H_3PO_4) activated, basic (10 % KOH solution) activated carbons produced from Nipa Palm (Nypa Fruticans Wurmb) and Commercial Activated Carbon (CAC) used as the control.

Materials and Methods

Nipa Palm Sample Collection and Processing: Fresh fronds of Nipa palm (Nypa fruticans Wurmb) were collected during low tide at the Ogbunabali waterfront along Eastern Bypass in Port Harcourt, Nigeria. Samples were washed with plenty of water to remove surface impurities and sun dried followed by oven drying at 110 °C for several days. Dried leaves were grounded and sieved to mesh size 106 µm to obtain the dried leaves biomas.

Preparation of physically carbonized carbon (PCC): About 25±0.01 g of the Nipa palm leaves biomass (<110 mesh size) was mixed with 25 ml of distilled water in a 1:1 ratio to form a paste. The paste was transferred was placed in a muffler furnace (Carbolite Sheffield England, LMF4) and was heated gradually to 550 °C for 10 min and allowed to remain at this temperature for 2 hrs and then poured into a bowl containing some ice block crystals. Excess water was drained and samples sun dried (Adowei and Abia, 2016; Gimba et al., 2004). Surface ash was removed by washing with 10% HCl, followed by rinsing with distilled water to remove residual acid (Adowei and Abia, 2016; Fan et al., 2003) until a pH 7±0.5 was ascertained. The solids were sun dried, followed by oven drying at 100 OC to constant-weight and sieved with fractions <106 µm were collected for use as physically carbonized carbon (PCC).

Preparation of Acid Activated Carbon (AAC): About 25±0.001g Nipa palm leaves biomass was placed in a beaker containing 25 ml of 10% (3.27 M) H3PO4 solution and thoroughly mixed and heated to form a paste. The paste was heated gradually to 500 °C for 10 min in a furnace, then, allowed to cool to room temperature. Surface ash was removed by washing with 10% HCl, followed by rinsing with distilled water to remove residual acid (Adowei and Abia, 2016; Fan et al., 2003) until a pH 7±0.5 was ascertained. The solids were sun dried, followed by oven drying at 100 °C to constant-weight and sieved with fractions <106 µm were collected for use as Acid Activated Carbon (AAC).

Basic Activated Carbon (BAC): 25±0.001g 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 paste was heated gradually to 500 °C for 10 min in a furnace, then, allowed to cool to room temperature. Surface ash was removed by washing with 10% HCl, followed by rinsing with distilled water to remove residual acid (Adowei and Abia, 2016; Fan et al., 2003) until a pH 7±0.5 was ascertained. The solids were sun dried, followed by oven drying at 100 °C to constant-weight and sieved with fractions <106 µm were collected for use as Basic Activated Carbon (BAC).

Commercial Activated Carbon (CAC): The commercial activated carbon AquaNuchar SA-1500 was used as the control.

Preparation of 2-(N,N-Dimethyl-4-aminophenyl)-azo-benzene carboxylic acid (DMABA) Solutions: A 1.0 g of water soluble Na-salt of DMABA crystals were dissolved in 300 ml distilled water and diluted to 1000 ml. 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 (CODi) and the COD of the distilled water was determined to give the blank COD.

Preparation of 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 (CODi). The COD of the 90, 80, 70, 60 and 50 ml isopropanol were also measured and considered to give the blank COD. The COD of the working solutions were measured as the initial COD (CODi) and the COD of the isopropanol was determined to give the blank COD.

Preparation of n-Propanol Solutions: 20, 40, 60, 80, and 100 ml of n-propanol were measured into five different beakers. 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 (CODi) and the COD of the distilled water was determined to give the blank COD.

Determination of effect of carbon dosage at 30°C: 0.2, 0.4, 0.6, 0.8, and 1.0 g of PCC, AAC, BAC of 106-µm mesh particle size and CAC were weighed and transferred into several 150 ml plastic sample container. 50 ml of DMABA, kerosene and n-propanol was added to each plastic sample container. The containers were tightly covered and shaken for 1 hour at 150 rpm. At the end of 1 hour, the suspensions were allowed to stand on the bench for 30 minutes to separate and then filtered using Whatman No 40 filter paper. The clear supernatant SOC solutions were analyzed for final COD (CODf).

Determination of Chemical Oxygen Demand (COD): 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 Eq. (1).

$$\text{COD as mg O}_2\text{/L} = \frac{(A-B)\ x\ m\,x\ 8000}{V_s} \qquad \text{Eq. (1)}$$

Where, A=ml of ferrous ammonium sulphate (FAS) used for blank; B=ml of FAS used for sample; M=molarity of FAS; Vs=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 Eq. (2).

$$\%\ \text{COD Removed} = \frac{\text{COD}_\text{i} - \text{COD}_\text{f}}{\text{COD}_\text{i}}\ \text{x}\ 100 \qquad \text{Eq. (2)}$$

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

Triplicate analysis ere carried out and the mean, standard deviations, standard errors and analysis of variance (ANOVA) were computed.

Results and Discussion

Effect of carbon dosage on COD reduction

The measured quantity of an adsorbent used to contact aqueous solution has a significant effect on the adsorption process. Several investigations (Tarawou et al., 2010; Kadirvelu et al., 2000) has revealed that, the larger the weight of the adsorbent, the greater the number of sorption sites available, adsorbent porosity and surface area thereby enhancing the adsorption capacity due to the number of available adsorption sites. Within the limit of experimental error and for economic reasons, the optimum weight of PCC, AAC and BAC were evaluated for the percent COD reductions of DMABA, kerosene and n-propanol. The consequence of carbon dosage on the COD reduction of DMABA solution is presented in *Figure 1*. The result showed that, percent COD reduction by PCC, AAC, BAC and the CAC increased with increase in carbon dosage with maximum carbon dosage obtained around 0.8g/50ml. This optimum amount of 0.8 g is capable of reducing COD level by 93.1%, 93.7%, 95.1%, and 96.6%, of DMABA by PCC, AAC, BAC and CAC at 30oC respectively.

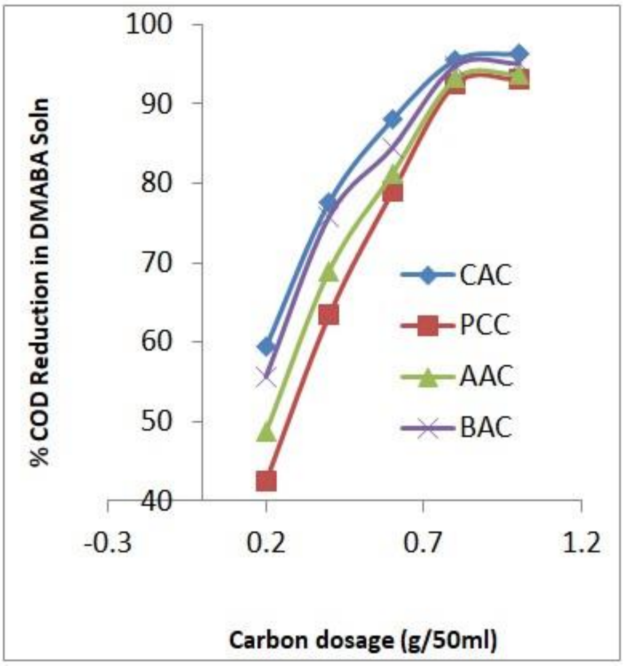

Figure 1. *Effect of carbon dosage on COD reduction of DMABA solution by PCC, AAC, BAC and CAC at 30°C.*

The reduction in COD content for kerosene as a function of carbon dosage is presented in *Figure 2*. The data indicates that COD reduction by the three carbons produced from Nipa palm leaves and the commercial activated carbon continue to increase all through the study limit and there was no effective optimum carbon mass obtained for the solutions investigated. The result for kerosene showed that COD reduction due to carbon dosage ranged from 25.5%-64.6%, 19.8%-55.8%, 20.5%-58.7% and 22.5%-61.4% by PCC, AAC, BAC and CAC respectively. The maximum COD reduction observed for kerosene was less than 65%.

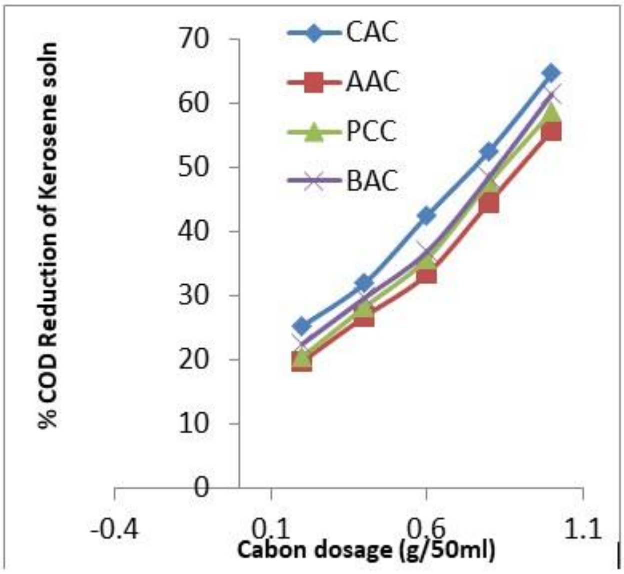

Figure 2. *Effect of carbon dosage on COD reduction of kerosene solution by PCC, AAC, BAC and CAC at 30°C.*

The decrease in initial COD content of n-propanol solution by PCC, AAC, BAC and CAC were studied by changing the quantity of adsorbent (0.2, 0.4, 0.6, 0.8 and 1.0 g/50 ml) in the test solution while keeping the initial SOCs concentration (100 mg/L), temperature (29 ±1 °C) and pH (6.7) constant. Experiments were carried out at different contact times for 60mins. As shown in *Figure 3*, the percent COD reduction measured increased with increasing adsorbent doses. The percent COD reduction increased from 11.5 to 64.7% for PCC, 9.3 to 62.5% for AAC, 17.5 to 72.2% for BAC and 12.2 to 74.5% for CAC. Comparative analysis of the COD reduction as a function of the carbons produced from Nipa palm and CAC showed that, BAC gave optimum removal of DMABA, kerosene and n-propanol.

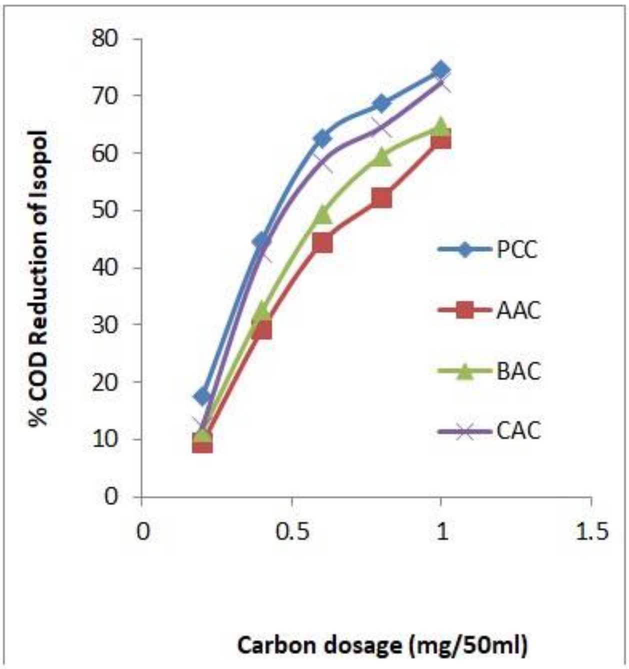

Figure 3. *Effect of carbon dosage on COD reduction of n-propanol solution by PCC, AAC, BAC and CAC at 30°C.*

The effect of carbon dosage of synthetic organic compounds removal in aqueous solutions by carbonized and surface-modified carbons from fresh nipa palm fronds reveals that increase in carbon dosage increases the percent removal until at a maximum carbon dosage obtained around 0.8g/50ml. Thereafter, a decrease in percentage was obserbered, this might be due to the fact that all active sites were entirely exposed at lower doses, while only a fraction of the active sites were exposed at higher doses. Thus, a higher adsorbent dosage may cause aggregation, which decreases the adsorbent, leading to a decrease in adsorption.

Conclusion

In conclusion, the series of batch adsorption experiments conducted in this work reveal that Nipa palm derived carbons are capable of reducing organic contaminants in aqueous solutions. Production of carbons from the leaves of Nipa palm is feasible, economical and environment friendly. These removal potentials are significantly comparable to the commercial activated used to validate the carbons. The feasibility was further assessed by using separation factor; and the data obtained revealed that the interaction between the Nipa palm derived carbons and the various 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.

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Conflict of interest

The authors confirm that there is no conflict of interest involve with any parties in this research study.

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