REMOVAL OF LOW CONCENTRATION OF KEROSENE FROM WATER USING NIPA PALM (NYPA FRUITICANS WURMB) FRUIT FIBRE

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ABSTRACT

Nipa palm fruit fibre was carbonized at 400°C in a muffle furnace and used to remove kerosene in contaminated water in a batch experimental process with chemical oxygen demand (COD) reduction as the measurement parameter. The elimination of kerosene in the contaminated water was studied by applying the effect of carbon dosage and initial contaminant concentration. The results obtained showed that, the best process conditions for removing kerosene in the contaminated water samples were 8.0 mg carbon dosage at low concentration of 20 mg/L of kerosene contamination. The adsorption isotherm of the elimination process was evaluated by Langmuir and Freundlich isotherm models and the data fitted better to Freundlich isotherm (R2 = 0.84) when compared to Langmuir isotherm (R2 = 0.88). The maximum monolayer surface coverage as computed from the Langmuir equilibrium adsorption data was 1.43 mg/g. The overall outcome indicates that the carbonized carbon produced from Nipa palm fruit fibre has low ability in reducing kerosene from contaminated water.

1. INTRODUCTION

Oily by-products are the most commonly encountered water contaminants in the Niger Delta region of Nigeria due to incessant artisanal and small-scale refining of crude oil in the region (Horsfall and Abia 2003). These contaminants may be present in solution in emulsified form, dissolved, or floating films and they are capable of representing a substantial threat to almost all organisms living in the region of the polluted water bodies or areas. The four classes of oily contaminants found in contaminated waters are [1] light hydrocarbons; [2] heavy hydrocarbons; [3] lubricants and cutting fluid; and [4] fats that are found in both plants and animals. The light hydrocarbons include gasoline, kerosene and jet fuel. Kerosene which is one of the fractions obtained from fractional distillation of crude oil is an important heating fuel and the most frequently detected water contaminant in the Niger Delta region of Nigeria (Adowei et al., 2014; Isiuku et al., 2013) where drinking-water sources rely heavy on...
borehole sources. Kerosene is a thin, clear liquid obtained from fractional distillation of petroleum between 150 deg C and 275 deg C, with typical density between 0.78 and 0.81 g/cu cm. It is a mixture of aliphatic compounds with carbon chains usually between 6 and 16 carbon atoms per molecule. Consequently very stringent standards are required for the regulation of oily contaminants in drinking water and water meant for disposal.

Numerous standards and regulations were adopted for discharge of oily waste water into surface water or sewage systems. These regulations vary from one country to another, and even within a country itself. Environment Canada (1976b) established a discharge limit for oil and grease of 15 mg/L at Federal establishment. The allowable oil and grease concentration for discharge into water in Iraq is 10 mg/L (Sulaymon and Ali, 2010), while in Nigeria the allowable limit is placed at 10 mg/L (FEPA, 1996). However, due to frequent crude oil and hydrocarbon products pollution in the Niger Delta area, several boreholes in communities has been reported to contain oily sheen with kerosene like smell.

Hydrocarbon oily products possess a strong unpleasant odors, and even at low concentrations such water cannot be used for drinking or for industrial purposes. Hydrocarbons differ from other pollutants in that they can easily penetrate living tissues and accumulate in various body organs. Oil pollution also represents a threat to man as the hydrocarbons enter the body via water and food product. Therefore it is necessary to ensure that, no trace of oily product is found in drinking water. Analytical techniques for removal of these pollutants generally involve biological degradation, chemical oxidation, physical stripping and adsorption process (Prather, 1970). Adsorption techniques are widely used in the field of removing small quantities of pollutant present in the large volume of fluid, which can be carried out in batch-wise or continuous manner of operation (Rao, 1994). Adsorption is based on the preferential uptake of pollutants in the force field in adsorbent pores and it is effective throughout the concentration range for a dissolved pollutant, but its advantages are prominent most fully over other methods at low concentrations. Oil products dissolved in water are efficiently adsorbed by activated carbon, but their use are hindered by high cost. To reduce the cost of sorbents, often activated carbon from agro-wastes or non-useful biomaterials are employed.

In this research, a Nipa palm plant which at the moment is depleting the more useful mangrove trees in the Niger Delta was used to produce the adsorbents. The production of activated carbons from agro-wastes has potential economic and environmental impacts. First, it converts unwanted, low-value agro-waste to useful, high-value adsorbents. Second, activated carbons are increasingly used in water treatment to remove organic chemicals and metals of environmental and/or economic concern.

At the moment, there are very few studies (Adowei et al., 2014) on the use of activated carbon produced from different parts of the Nypa fruticans plant as adsorbent for removal of organic contaminant in aqueous solutions. In this paper we report the removal of kerosene in water contaminated with minute amount of kerosene using carbonized carbon made from Nipa Palm (Nypa Fruiticans Wurmb) Fruit Fibre in a batch adsorption process using chemical oxygen demand (COD) as the index of measurement.

2. MATERIALS AND METHODS

2.1. SAMPLE COLLECTION

Fresh fruit of Nipa palm plants were collected during low tide at the Ogbunabali waterfront along Eastern Bypass in Port Harcourt, Nigeria and taken for taxonomical identification. The Nipa Palm fruit were air dried and the fibre carefully removed. The fibre was oven dried at 80°C for several days, cut into small sizes, which were further oven-dried, grounded and sieved with a 150 µm mesh size sieve to obtain the uniform sized biomass sample. The dried biomass sample was carbonized in Plant Science and Biotechnology Laboratory of the University of Port Harcourt, Nigeria.

2.2. PREPARATION OF CARBONIZED CARBON FROM NIPA PALM FRUIT FIBRE

100g of the sample was taken and weighed into a porcelain crucible. The porcelain crucible is then fixed into a muffle furnace, the adjustment knob was selected at a temperature of 400°C and the muffle furnace was left on for a period of 1hr. The carbonized nipa fruit fibre was fixed in desiccators to cool so as to avoid air (so as to avoid oxidation from taking place).
2.3. PREPARATION OF SYNTHETIC KEROSENE CONTAMINATED WATER

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 100ml volumetric flasks. The mixtures were thoroughly shaken by a shaker. The COD of these mixtures were measured as initial COD ($C_{ODi}$).

2.4. BATCH ADSORPTION STUDIES

2.4.1. DETERMINATION OF EFFECT OF CARBON DOSAGE

2, 4, 6, 8, and 10 g of finely divided nipa palm fruit fibre with uniform particle size of 106-µm were separately placed in a series of 75 ml plastic sample containers containing 50 ml of 100 mg/l concentration of kerosene solution. The suspensions were shaken at room temperature using agitation speed of 150 rpm for 60 min. At the end of 60min, Ten ml from each sample was taken and mixed with 10 ml of iso-propyl alcohol (extra pure) as co-solvent (Bastow et al., 1997) and the mixture was shaken by the shaker (type: Stuart scientific, Auto vortex SA6, UK) for 2 min, and centrifuged at 1000 X. The COD of the clear supernatant solutions were determined by multi-parameter bench photometer with Tungsten light source at 420nm.

2.4.2. DETERMINATION OF EFFECT OF INITIAL CONCENTRATION

Solutions were prepared containing the desired kerosene concentration of 20, 40, 60, 80, and 100 mg/L. 100 ml of each prepared solutions were placed in plastic bottles each of 250 ml capacity. 2.0 g of finely divided nipa palm fruit fibre with uniform particle size of 106-µm were separately placed in the individual bottles with another bottle containing the same quantity of adsorbent and distilled water serving as a blank. The bottles were then placed on a shaker (Type: Stuart scientific, Auto vortex SA6, UK) and agitated continuously for 60 min at room temperature using agitation speed of 150 rpm. Ten ml from each sample was taken and mixed with 10 ml of iso-propyl alcohol (extra pure) as co-solvent (Bastow et al., 1997) and the mixture was shaken by the shaker (type: Stuart scientific, Auto vortex SA6, UK) for 2 min, and then centrifuged at 1000 x g).

The clear supernatant solutions were used for determination of COD using multi-parameter bench photometer (Model: HI 83099) with Tungsten light source at 420nm.

2.4.3. PROCEDURE FOR MEASUREMENT OF CHEMICAL OXYGEN DEMAND (COD)

2.50 ml centrifuged clear supernatant solution was added to the Reagent vials and 2.50 ml of deionized water was added to another vial as blank. This was followed by slowly adding 2.50 ml standard potassium dichromate digestion reagent and then mixed. Then a 3.5 ml sulfuric acid reagent was added through the sides of the tubes and allowed to go down to the bottom. The content was capped and mixed and allowed to cool. The tubes were then transferred to the pre-heated COD digester at 150 ºC and digested for 2 hrs. Thereafter, each vial was inverted several times while still warm, they were then placed in the test-tube rack. The vials in the tube rack were left to cool to room temperature. At this point, there was no shaking or inversion so that the samples were not turbid. The concentration in mg/L of oxygen demand was then measured for both blank and samples.

2.4.4. ANALYSIS OF EXPERIMENTAL DATA

The amount of kerosene removed from contaminated water at equilibrium by the biomass was calculated by the mass balance relationship (Adowei et al., 2015).

$$q_e = \frac{(C_o - C_e)V}{w}$$
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Where
\[ q_e = \text{amount of kerosene removed from contaminated water by carbon (mg/g)} \]
\[ C_o = \text{initial concentration of kerosene contaminated water before contact with carbon} \]
\[ C_e = \text{equilibrium concentration of kerosene contaminated water after contact with carbon} \]
\[ V = \text{volume of kerosene contaminated water used (L)} \]
\[ w = \text{weight of the nipa fruit fibre carbon used (g)} \]

The experimental data were analyzed by the two commonly used adsorption isotherm models of Langmuir and Freundlich.

The Langmuir equation is expressed as:
\[ q_e = \frac{q_m k_L C_e}{1 + k_L C_e} \]

Where \( k_L (\text{dm}^3\text{g}^{-1}) \) is a constant that is related to the adsorption/desorption energy, and \( q_e \) is the maximum sorption on complete saturation of the adsorbent surface. Linearization of the above equation gives
\[ \frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m} \]

A plot of \( C_e/q_e \) against \( C_e \) gives a straight-line curve with slope \( \frac{1}{q_m} \) and intercept \( \frac{1}{q_m k_L} \).

The Freundlich isotherm shows the adsorption intensity of the adsorbate on the adsorbent and has a purely empirical formula
\[ q_e = \frac{x}{m} = k_f C_e^{1/n} \]

Where \( q_e \) is the adsorption density (mg/g), \( x \) is the adsorbed quantity (mg) \( m \) is the mass of adsorbent (g), \( C_e \) is the concentration of the adsorbate in solution at equilibrium (mg/dm^3), \( K_f \) and \( n \) are the Freundlich constants.

According to Horsfall and Abia (2003), the value of \( n \) shows the affinity of the adsorbate towards the adsorbent. The linearised form of the Freundlich equation is;
\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]

If a plot of \( \log q_e \) against \( \log C_e \) yeilds a straight line, then the sorption process obeys a Freundlich adsorption isotherm. The \( K_f \) and \( \frac{1}{n} \) can be obtained from the intercept and slope of the straight line.

3. RESULTS AND DISCUSSION

3.1. EFFECT OF CARBON DOSAGE ON THE REMOVAL OF KEROSENE FROM WATER

The result obtained for the effect of carbon dosage on the removal of kerosene from the contaminated water using the carbonized carbon produced from the Nipa palm fruit fibre measured as percent removal of chemical oxygen demand (COD) is presented in Figure 1.

The data revealed that the percent (%) COD reduction from the kerosene contaminated water as a result of carbon dosage were 36.84% for 2 mg/L carbon dosage, 51.06% for 4 mg/L, 56.06% for 6 mg/L carbon dosage, 66.44% for 8 mg/L carbon dosage and 61.65% for 10 mg/L carbon dosage respectively. The result showed that, COD reduction increased as the carbon dosage increased until a maximum reduction was obtained at 8.0 mg/L of carbon dosage. The maximum COD reduction observed for was 66.44%.

The quantity of the adsorbent material to contact the adsorbate in aqueous solution has a significant effect on the adsorption process. Several authors (Kapadia et al., 2000, Tarawou et al., 2007) has revealed that, the larger the
weight of the adsorbent, the greater the number of sorption sites available. This will increase the adsorbent porosity and surface area thereby enhancing the adsorption capacity due to the number of available adsorption sites.

![Figure 1](image1.png)

**Figure 1:** Effect of carbon dosage on COD reduction of kerosene contaminated water by carbon from Nipa palm fruit fibre

### 3.2. EFFECT OF INITIAL CONCENTRATION ON KEROSENE REMOVAL FROM WATER

The COD reduction capacity of the Nipa palm fruit fibre carbon for various initial concentration of kerosene in the contaminated water was also studied and the result is presented in Figure 2. The data showed that the ability of the sample to reduce COD is higher at lower concentration of kerosene contaminated water. From the figure, it was observed that, the percent of COD reduction which measures the adsorption efficiency of the carbons decreased with increase in initial kerosene concentration in the water. The reason may be that as the concentration of kerosene is increasing, the adsorption sites are easily taken up and more of the kerosene is unable to be removed.

![Figure 2](image2.png)

**Figure 2:** Effect of initial concentration of kerosene in contaminated water
3.3. ADSORPTION ISOTHERMS DATA ANALYSIS

In order to estimate practical capacity, the COD reduction data obtained from the experiment were used to calculate the Langmuir and Freundlich model parameters. Langmuir equation was chosen to estimate maximum COD reduction capacity corresponding to monolayer coverage on the carbon surface. The sorption isotherms of COD reduction of kerosene contaminated water by Nipa palm carbon were fitted by the Langmuir and Freundlich models, as shown in Figure 3 and Figure 4.

Figure 3: Langmuir isotherm model plot of COD reduction of kerosene contaminated water by carbon

The Langmuir constants $q_{\text{max}}$, $K_L$, and the Freundlich constants $K_F$, $n$ showed in these results were determined by linear regression and found to be 1.4286, 9.214 and 8.97 x 10^{-7}, 5.14 respectively and the regression coefficients ($r^2$) are 0.842 for Langmuir and 0.876 for Freundlich. These values suggest that the COD reduction of kerosene in contaminated water can be modelled by Langmuir as well as Freundlich model with a slight preference to Freundlich.

Figure 4: Freundlich isotherm model plot of COD reduction of kerosene contaminated water by carbon
The values of the Langmuir parameters $q_{\text{max}}$, $K_L$, and Freundlich parameters $K_F$, $n$ and the calculated regression correlation coefficients ($R^2$) were reported in Table 1.

Table 1: Langmuir and Freundlich isotherm parameters computed from the regression equations for COD reduction by Nipa palm carbon

<table>
<thead>
<tr>
<th>Langmuir Model Parameters</th>
<th>Freundlich Model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>$K_L$ (L/g)</td>
</tr>
<tr>
<td>1.4286</td>
<td>9.214</td>
</tr>
<tr>
<td>$R^2$</td>
<td>$n$</td>
</tr>
<tr>
<td>0.842</td>
<td>5.14</td>
</tr>
<tr>
<td>$K_F$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>8.97 x 10^{-7}</td>
<td>0.876</td>
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</table>

The Langmuir monolayer COD reduction capacity of Nipa palm biomass for methyl red in aqueous solution was estimated as 1.4282 mg/g. Adowei et al. (2014) however, found that the COD reduction for some synthetic organic chemicals (SOCs) onto carbonized and surface-modified carbons produced from Nipa palm leaves followed Langmuir model. It can be seen that Nipa palm biomass is an effective adsorbent for the reduction of chemical oxygen demand (COD) for organic contaminants in aqueous solution, when compared with some other adsorbents.

The Langmuir data was further used to evaluate the favourability of the COD reduction process of methyl red solution by Nipa palm biomass. The dimensionless parameter of the equilibrium adsorption intensity ($R_L$) can be expressed as

$$R_L = \frac{1}{1 + K_L C_o}$$

Where $C_o$ (mg/L) is the initial concentration of the methyl red solution and $K_L$ (L/mg) is the Langmuir constant related to the energy of adsorption. The value of $R_L$ indicates the shape of the isotherms to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The influence of isotherm shape on whether adsorption is favorable or unfavorable has been considered (Zacar and Engil, 2004). For a Langmuir type adsorption process, the isotherm shape can be classified by a dimension less constant the Separation factor ($R_L$), given by the Equation above. The calculated $R_L$ value at an initial methyl red concentration of 100 mg/L was obtained as 0.097. It was observed that this value of $R_L$ is in the range 0 - 1 which confirmed that there is a favourable removal of methyl red from the aqueous solution. The degree of favourability is generally related to the irreversibility of the system, giving a qualitative assessment of the biomass–methyl red interactions. The degrees of favourability in this study revealed that biomass–methyl red interactions is irreversible.

4. CONCLUSION

This study has successfully explored the equilibrium behavior of the production and application of carbonized carbon from Nipa palm fruit fibre for the removal of low concentrations of kerosene found in water samples from the Niger Delta region of Nigeria using reduction of chemical oxygen demand as the index of measurement. The study has provided data for the enlistment of carbonized Nipa palm fruit fibre as a potential and novel adsorbent for the reduction of low concentration of organic contaminates in water and may be recommended for industrial treatment of low hydrophilic organic effluents.

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None.

CONFLICT OF INTEREST

None.
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REFERENCES


