SEPARATION OF DISPERSED OIL IN PRODUCED WATER USING ACETYLATED *LUFFER CYLINDRICA* AS BIOSORBENT

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Abstract
The disposal of untreated produced water into water ways from oil recovery activities by oil and gas industries especially in the Niger Delta region is alarming. Separation of dispersed oil in produced water remains a challenge to environmental scientist. Sorption is a popular technique for clean-up of oil on aqueous media. In this study, luffa cylindrica, which are abundant, biodegradable agricultural product with less usage in Nigeria, were modified with acetic anhydride to increase their hydrophobic properties and improve their oil sorption effectiveness in aqueous environments. The un-acetylated luffa cylindrical, UALC and the acetylated luffa cylindrica, ALC were both characterized for chemical composition (AAS), functional group (FT-IR) and mineralogical (XRD). The result shows that the dispersed oil sorption efficiency of the acetylated luffa cylindrica, ALC was enhanced by 60% as compared with 40% for the un-acetylated luffa cylindrica, UALC. The results presented and discussed in this study also indicated that the rapid uptake and high absorption capacity of the ALC make it a very promising alternative sorbent for oil industries since the material is cheap, biodegradable and environmentally friendly.

Keywords: Dispersed oil; Acetylated luffa cylindrica; Oleophilic; Sorption efficiency.

1.0 Introduction
The need for Environmental pollution control is one of the most important issues that needs immediate attention due to the problems facing humanity and other life forms on our planet today (Guerra et al., 2011). During oil explorations and production process, produced oil usually comes with produced water and the amount of water in the produced oil must be reduced to accepted limits, and as exploited reservoir mature, the quantity of produced water discharge increases (Cox, 1992). Additional water is often injected into the reservoirs in order to achieve maximum oil recovery (Annunciado et al., 2005). Produced water Reinjection for enhanced recovery or disposal accounts for as much as 95% of this water (Ohimain, 2003). All produced water contains dispersed oil; the organic components of produced water include three different types of oil: dispersed oil, dissolved oil and free oil. The Free oil is easily removed from the aqueous phase; dispersed oil refers to small oil droplets suspended in the aqueous phase of the produced water (Sullivan et al., 2004). Both the dispersed oil and dissolved oils are not separated by the treatment process but are usually discharged into the ocean with the water. One of the immediate physical environments that suffer the direct impact of produced water disposal is the offshore (Gbadebo, et al., 2010). Due to produced water destructive properties, entire character of an area is damaged once contaminated with the oily produce water. Oil endangers fish at cherries in coastal areas and contaminates the...
flesh of commercially valuable fishes (Nwankwere et al., 2010). Therefore it is very important that the dispersed oil in the produced water must be separated before the water can be disposed or used for other economic purposes because contaminated water cannot be used for municipal water supply, in industry, or irrigation purpose. However, with appropriate treatment technique, produced water can serve as a new water supply (Guerra et al., 2011).

Sorption technique is one of the most effective approaches for oil cleanup. Among the various sorbents that have been employed for remediation, synthetic materials (such as polypropylene and polyurethanes) are the most commonly used commercial sorbents due to their oleophilic and hydrophobic properties (Teas et al., 2001). Unfortunately, most of these materials are not biodegradable and environmentally unfriendly. These characteristics fall among the disadvantages (Choi and Cloud, 1992). Therefore, there is a renewed interest in natural sorbents and a wide variety of organic vegetable products (such as rice straw, peat moss, wood, and cotton etc.) employed as bio-sorbents for oil clean-up (Deschamps et al., 2003). The main drawbacks of these plant-derived sorbents are their relatively low oil sorption capacity, low hydrophobicity and poor buoyancy compared to synthetic sorbents (Bayat et al., 2005). Agricultural products have well-documented problems with water sorption and lack dimensional stability due to their associated hydroxyl functionalities and these groups are responsible for their hydrophilicity (Nwadiogbu et al., 2014). Researchers have made several efforts to increase the hydrophobicity and oleophilicity of cellulose-based biopolymers by physical, chemical, and thermal modifications (Teas et al, 2001). The effectiveness of the sorbents in saturated environments can be enhanced when the density of the hydroxyl functionalities is decreased (Bodirlau and Teaca, 2009). Chemical modifications which can reduce the hydroxyl functionality of these agricultural fibers is by acetylation, methylation, cyanoethylation, benzylation, acrylation and acylation (Rowell et al., 1990).

For the purpose of this research work, *Luffa Cylindrica* a biodegradable agricultural product abundantly found in Nigeria and easily accessible, was employed as a precursor, where it was modified chemically by acetylation and the acetylated *Luffa Cylindrica* was used as a modified bio-sorbent material to separate dispersed oil in the produced water from oil production and the kinetics of the dispersed oil sorption by the acetylated *Luffa Cylindrica* was studied.

**2.0 Materials and methods**

i. 1000 cm$^3$ (1Liter) of Produced water Sample was collected directly from an international oil company operating in Nigeria for the purpose of the experiment.

ii. *Luffa cylindrica* was collected at Kagoro, Kaura local government Area of Kaduna state, Nigeria.

iii. Acetic anhydride, N-bromosuccinimide (NBS), aceton, ethanol and n-hexane were bought in Jos, Pleateau State of Nigeria and were used without further purification

**2.1 Material preparations**

The raw *luffa cylindrica* were collected and thoroughly washed with water to remove dust, fungus, foreign materials and water soluble components. The washed *luffa cylindrica* was dried under the sunlight for 12 hours (4 h for three days) and then left to dry at 65°C in an oven to remove the moisture content. It was crushed and sieved through 20 and 25 British standard sieves (BSS Sieves) prior to physicochemical analysis.
2.1.1 Soxhlet extraction
This was done to minimize the influence of the fibre extract on acetylation; 10 g of the sieved materials were extracted with a mixture of acetone and n-hexane (4:1, v/v) for 5 h. The extracted samples were dried in a laboratory oven for 16 h at 65°C to remove the moisture content before the modification process.

2.2 Acetylation of Luffa Cylindrica
The acetylation of the luffa cylindrica was carried out under mild conditions using acetic anhydride according to the method reported by Sun et al. (2004) which involved acetylation in a solvent-free system. The amount of substrate and reactant was combined in a ratio of 1:20 (g dried luffa cylindrica/mL acetic anhydride). The reaction temperature and time was 100°C and 1h respectively. The mixture of raw luffa sponge, acetic anhydride and catalyst will be placed in a round-bottom flask fitted to a condenser. The flask was placed in an oil bath on top of a thermo-static heating device. Then, the flask was removed from the bath, and the hot reagent was decanted. The luffa cylindrica was thoroughly washed with ethanol and acetone to remove unreacted acetic anhydride and the acetic acid by-products. The new products were dried in an oven at 60°C for 16 h prior to analysis according to Sun et al. (2004).

During the acetylation modification, the acetyl group from the acetic anhydride reacts with the hydroxyl group on the cellulose and hemicellulose to form oleophilic acetate groups (O–CO–CH₃) (Nwankwere et al., 2010)

\[
\text{LC-OH + CH₃-C(=O)-O-C(=O)-CH₃} \rightarrow \text{LC-O-C(=O)-CH₃ + CH₃-COOH}
\]

Reactant decomposition product formation

\[
\text{LC}^{+} \text{OH}^{-} + \text{CH₃-C(=O)=O-C(=O)-CH₃} \rightarrow \text{LC-O-C(=O)-CH₃ + CH₃-COOH}
\]

Hydroxyl group Acetyl group → Oleophilic LC acetate + Ethanoic acid

\[
\text{CH₃-COOH + CH₃CH₂OH} \rightarrow \text{CH₃COOCH₃CH₂ + H₂O}
\]

Bye product and organic base Decomposition

\[
\text{CH₃-COO}^{-} + \text{H}^{+} + \text{CH₃CH₂OH} \rightarrow \text{CH₃COOCH₃CH₂ + H₂O}
\]

Ethanoic acid Ethanol Ethylethanoate water

2.3 Physicochemical characterization
The Fourier Transform Infrared spectroscopy (cary 630 FTIR), X-ray diffraction, XRD analysis were carried out on both the Un-acetylated Luffa Cylindrica, UALC and the Acetylated Luffa Cylindrica, ALC.

2.4 Treatment procedure
The sorption of oil from produced water was carried out using the methods reported by Banerjee et al. (2006). A portion 1g of Unacetylated luffa cylindical, UALC and acetylated luffa cylindical, ALC each were placed in a 250-mL beaker containing 100mL of produced water at room temperature. The samples were left in the mixture for approximately 2 min with little agitation. The sorbents were removed from the beakers using sieve nets. The sieve nets were allowed to drain. The oil-loaded sorbents were dried at 60°C for 30 min and re-weighed and the oil sorption capacity was calculated by taking into account the weight of the sorbent, the weight of the sorbent and oil and the weight of sieve net.

\[
\text{Oil sorption capacity (g/g)} = \frac{\text{Sst}-\text{So}}{\text{So}} \quad --- \ (1)
\]

Where So is the initial mass of the dry sorbent,
$S_{st}$ is the mass of the sorbent with oil at the end of the sorption test and the $(S_{st} - S_{o})$ quantity is the net oil adsorbed (all of the masses were measured in grams).

The amount of crude oil adsorbed ($q_e$) in milligrams per gram were determined using the following mass balance equation:

$$q_e = \frac{(C_o - C_e)V}{m} \quad --- (2)$$

Where $C_o$ is the initial oil concentration in mg/L,

$C_e$ is the equilibrium oil concentration in mg/L,

$V$ is the volume of the solution in liters, and

$m$ is the mass of the adsorbent in g.

3.0 Result and Discussion
3.1 Mineral composition
The results of the mineral composition of the raw *luffa cylindrica* determined from AAS are shown in Table 1 below. The results confirm that the material contained a high quantity of P, Mg, K, Na and very little percentage of Cr. These minerals contribute to the hydrophilic characteristic nature of the material.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus (mg/100g)</td>
<td>30.63</td>
</tr>
<tr>
<td>Magnesium (mg/100g)</td>
<td>28.93</td>
</tr>
<tr>
<td>Potassium (mg/100g)</td>
<td>13.89</td>
</tr>
<tr>
<td>Sodium (mg/100g)</td>
<td>8.18</td>
</tr>
<tr>
<td>Chromium (mg/100g)</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The results of the physical properties of the un-acetylated *luffa cylindrica* UALC are presented in Table 2 below. The moisture content reported in this study falls within an acceptable limit of 5%. The moisture content (<5%) is needed to achieve optimal acetylation, the values above this level result in hydrolysis of anhydrides to their corresponding carboxylic acids, which accounts for a 5.7% loss of anhydrides for every 1% of water in the wood, this finding is in agreement with the findings of Bodirlau and Teaca (2009).

<table>
<thead>
<tr>
<th>Property</th>
<th>(wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (g/mL)</td>
<td>1.2</td>
</tr>
<tr>
<td>Porosity</td>
<td>38</td>
</tr>
<tr>
<td>Moisture content</td>
<td>5</td>
</tr>
<tr>
<td>Cellulose</td>
<td>63</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>15</td>
</tr>
<tr>
<td>Lignin</td>
<td>10</td>
</tr>
</tbody>
</table>

3.4 Fourier Transform Infra-Red (FTIR) Spectroscopy
The FTIR spectrum result of a raw *luffa cylindrica* is shown in Fig 1(a); the bands in the region of 3320 cm$^{-1}$ indicate the presence of a stretching of strong hydroxyl groups which contribute to the hydrophilic nature of the un-acetylated *luffa cylindrica*. The band at
2900 cm\(^{-1}\) is assigned to C-H stretching. Also the band at 1705 cm\(^{-1}\) corresponds to the stretching of a carbonyl C=O (hemicellulose band). The band at 1610 cm\(^{-1}\) represents absorbed water and the band at 1380 cm\(^{-1}\) is assigned to −C−H bonding. In addition, the band at 1258 cm\(^{-1}\) corresponds to C-O stretching (lignin band) and the band at 1019 cm\(^{-1}\) represents C-OR stretching. The presence of the stretch strong hydroxyl groups in the Un-acetylated \textit{luffa cylindrica} have made it absorb much water and less oil in the dispersed oil sorption process and easily decomposes thereby rendering it not effective for use.

From FTIR spectrum pattern of the Acetylated \textit{luffa cylindrica} shown fig.1 (b); there is no longer band at the region of 3320 cm\(^{-1}\) which indicate that the stretched strong hydroxyl group previous in the un-acetylated \textit{luffa cylindrica} is replaced with acetyl group which is oleophilic, having more affinity to adsorb more oil than water and this is as a result of the acetylation modification of the \textit{luffa cylindrica}.

\textbf{Figure 1 (a): FTIR pattern of UALC & figure 1(b): ALC}
3.5 X-Ray Diffraction (XRD)

The XRD patterns of the UALC and the ALC are presented in Fig. 2. The two broad peaks that appeared at 15° and 20° in the crystalline pattern of the UALC are typical of the XRD pattern of alpha cellulose (Nwadiogbu et al., 2014). Peaks with significantly reduced intensity were observed in the pattern of the acetylated *luffa cylindrical*, ALC which indicated that the structure of the LC was transformed to an amorphous structure after acetylation. Acetylation of the cellulose material often results in a decrease in crystallinity (Kosaka *et al.*, 2005).
A major portion of cellulose is in a crystalline form due to intra- and inter-molecular hydrogen bonding of hydroxyl groups (Teas et al., 2001). These crystallites mainly have a hydrogen bond with hydroxyl groups and are attacked by acetic anhydride to form acetylated cellulose in the amorphous structure (Nwadiogbu et al., 2014). The substitution of an acetyl group for a hydroxyl group reduces the density of hydrogen bonding because an acetyl group offers a more bulky branch (i.e., a decreased ability to form hydrogen bonding) than a hydroxyl group. Therefore, the acetylated *luffa cylindrica* will possess more desirable properties for oil sorption in an aqueous environment.

3.6 Effect of Contact time on oil sorption capacity (OSC) of the LC

The effect of contact time is shown in table 4 below and the initial concentration, $C_o$ of the dispersed oil in the produced was determined to be $C_o=5000\text{mg/L}$, volume of solution $V=1\text{L}$, mass of adsorbent $m=1\text{g}$.

The amount of oil adsorb was calculated with the mass balance equation

$$q_e = \frac{(C_o-C_e)V}{m}$$  \(--- (2)\)

Where: $C_e$ is the equilibrium concentration of the dispersed oil in the solution after the separation process. The results are presented in table below.

![Figure 2; XRD patterns of UALC & ALC](image)
Table 3: contact time on OSC

<table>
<thead>
<tr>
<th>t(sec)</th>
<th>UALC C_t (mg/L)</th>
<th>UALC,OSC q_t (mg/g)</th>
<th>ALC C_t (mg/L)</th>
<th>ALC,OSC q_t (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3500</td>
<td>1500</td>
<td>3000</td>
<td>2000</td>
</tr>
<tr>
<td>60</td>
<td>3100</td>
<td>1900</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>90</td>
<td>2800</td>
<td>2200</td>
<td>2200</td>
<td>2800</td>
</tr>
<tr>
<td>120</td>
<td>2700</td>
<td>2300</td>
<td>2000</td>
<td>3000</td>
</tr>
<tr>
<td>150</td>
<td>2700</td>
<td>2300</td>
<td>2000</td>
<td>3000</td>
</tr>
</tbody>
</table>

At the end of the experimental time C_t =3000mg/L for the ALC and C_t =2700mg/L for the UALC.

Therefore the ALC % change in dispersed oil concentration (OS Efficiency) = \left( \frac{2000-5000}{5000} \right) * 100% = -60%.

The UALC % change in dispersed oil concentration (OS efficiency) = \left( \frac{2700-5000}{5000} \right) * 100% = -46%

![Effect of Contact Time](image)

**Figure 3: Effect of contact time on OSC**

Fig. 3 above shows the results for the effect of the sorption times on oil removal. As expected, the sorption capacity increased as the sorption time increased from 30 to 150s. A time of 150 s resulted in an optimum oil sorption capacity of 3.0 g/g for the acetylated *Luffa cylindrica*, ALC and 2.0 g/g for the Un-Acetylated *Luffa Cylindrica*, UALC.

The initial fast adsorption may be due to the initial adsorption onto the surface of the material and subsequent penetration into the inner microscopic voids (Dawodu F.A, Akpomie, 2014). The slow uptake in the later stages may be due to an attachment controlled process caused by less available sites for active sorption. In all of the studied time periods, the acetylated *Luffa cylindrica* absorbed more oil than the Un-Acetylated *Luffa cylindrica*; this may be due to the reduction in the water absorption capacity of the *Luffa cylindrica* resulting from acetylation, increasing its potential to sorb more oil in an aqueous medium with time. Therefore, the optimum time required is 150s. where ALC has a high oil sorption efficiency of -60% than the UALC with oil sorption efficiency of -46%.

### 3.9 Influence of Adsorbent Dose

Increase in adsorbent Dose either increases or decreases the adsorption. The influence of the adsorbent dose is shown in the table 4 below:

<table>
<thead>
<tr>
<th>Dosage(g)</th>
<th>UALC,OSC q(g/g)</th>
<th>ALC, OSC q(g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.0</td>
<td>2.5</td>
</tr>
<tr>
<td>1.0</td>
<td>2.2</td>
<td>2.9</td>
</tr>
<tr>
<td>1.5</td>
<td>2.4</td>
<td>3.2</td>
</tr>
<tr>
<td>2.0</td>
<td>2.6</td>
<td>3.4</td>
</tr>
</tbody>
</table>
Figure 4; Effect of Biosorbent dosage on the Oil sorption capacity of luffa cylindrica

As the mass of the sorbents increased from 0.5 g to 2.5 g, a corresponding increase in the oil sorption capacity was observed up to an optimum value of 3.4g/g with absorbent dosage of 2.0g; this is primarily due to an increase in the surface area as well as the availability of more active binding sites which is in agreement with the findings of Zafar et al. (2006), but at some point there was no further increase in adsorption even with the increase in the adsorbent dose which could be due to overlap of the adsorbent active site which limit the increase in adsorption with increasing adsorbent dose. Therefore the optimum quantity of adsorbent required is 2.0g for high adsorption capacity of 3.4g/g.

4.0 Conclusions
i. The study indicates that the LC physicochemical properties include porosity 38%, moisture content 9wt%, cellulose 68wt%, and hemicellulose 15wt% and hydroxyl functional group replaced with acetyl group after modification.

ii. The dispersed oil sorption efficiency of the ALC was enhanced to 60% of the initial oil concentration than UALC with 40% sorption efficiency

iii. Therefore the rapid uptake and high absorption capacity of the acetylated Luffa cylindrica, ALC makes it a very promising alternative sorbent for oil industry because this material is cheap and biodegradable.

REFERENCES
Dawodu F.A, Akpomie K.G, Simultaneous adsorption of Ni(II)and Mn(II) ions from aqueous solution unto a Nigerian


