Application of Esterified Ogbono Shell Activated Biomass as an Effective Adsorbent in the Removal of Crude Oil layer from Polluting Water Surface

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ABSTRACT: This work focuses on the removal of oil from polluted water surface using activated biomass such as ogbono shell. The shell was carbonized at a temperature of 600°C for 4h and then further modified with stearic acid. Characterization of the adsorbent produced was carried out using Scanning electron microscopy (SEM) to study the surface morphology of raw and grafted ogbono shell. Fourier Transform Infra-red Spectroscopy (FTIR) was used to investigated the functional group of different minerals. Proximate analysis was carried out to determine the surface area of the agro wastes before and after modification. Batch experiments were carried out to investigate the effects of the oil water ratio, temperature, pH and contact time on the sorption capacities of the adsorbents. Physiochemical characterization of the adsorbents revealed that surface area increased from 114 cm² to 190.5 cm² after modification. SEM and FTIR results revealed that more micro porous surfaces were created on the surface of the adsorbent after modification. Batch adsorption experiments with esterified ogbono shell revealed that 96% of crude oil was removed at a pH of 5 with oil water ratio of 1.4/100 cm² after 50 min at a temperature of 90°C. Esterified ogbono shell was found to be a good adsorbent for the removal of oil layer from polluting water surface.

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In recent times, water pollution of seas and underground water has been a growing concern for many countries most especially Nigeria. The major causes of pollution of water surface and underground water has been traced to oil spills (Baars, 2002). Oil spills could be due to release of oil or its derivatives like diesel, petrol, lubricating oil etc from tankers and underground pipes due to breakage occasioned by accident (Banerjee et al., 2006). Investigation on the use of agricultural waste (agro-waste) for the removal of oil from aqueous solutions has been on the increase. Some of these waste materials are available at no cost, naturally occurring, stable and require minimum care or maintenance (Ali et al., 2012; Annunciado et al., 2005). The use of agricultural adsorbents seems to have been recognized as an effective and remarkable control measure in many oil spill situations (Olufemi et al., 2014, Uzoije et al., 2011). Oil pollution of the water bodies and underground water requires urgent attentions due to their environmental and economic importance (Reza et al., 2013; Annunciado et al., 2005). Aquatic animal species respond differently to crude oil or its derivative products pollution in water. However, the crude oil spills in an aquatic environment floats and block out sunlight initiating the death of phytoplankton and seaweed, sources of food and indeed the chief sources of food chains, therefore causing starvation to lives living under the water (Uzoije et al., 2011; Gwendoline, 2010). Nowadays, there has been a tremendous attention regarding the treatment of water and polluted water has been on the increase. However, the most frequent method of water treatments including flocculation, ultra filtration, biological treatment and coagulation (Suidan et al., 2005; Ayotamuno et al., 2006; Yang et al., 2006) suffer from draw back such as high capital, operational cost, time consumption, equipment complexity and the disposal of the residual sludge and do not seem to be economically viable (Uzoije et al., 2011). Adsorption offers the best solution since the process is cheap and faster coupled with the fact that sophisticated equipment are not required for the experiments and the overall process is eco-friendly (Ilaboya et al., 2013) In recent years, natural and organic sorbents synthesized from peat moss, wood, cotton, rice straw, corncobks and kapoks have been identified as an effective sorbents in oil spill treatment (Nwadiogbu et al., 2016). Ogbono shell is an agro wastes gotten after
removing the ogbono seed. It is found mostly in southern part of Nigeria of which are predominantly in south east Nigeria. It is available at no cost. Therefore, this research is aimed at investigating the oil adsorption capacity of ogbono shell modified with organic acid.

MATERIALS AND METHOD

Materials: Ogbono shells were collected from Akpoga Nike in Enugu State Nigeria. The shells were first washed and dried under the sun for one week. After which, the shells were grinded using a commercial grinder at Oye Market in Emene, Enugu State. Other materials used included; Crude oil, distilled water, sodium hydroxide (NaOH), H₂SO₄, HCl, Sieving net, stearic acid, n-hexane.

Methods: Preparation of Carbonized Adsorbent (Ogbono Shells): The dried biomass (Ogbono shells) was carbonized in a muffle furnace at 600°C for 4h respectively. After the carbonization, the samples were cooled and stored in dry transparent containers for further use (Angelova et al., 2011).

Modification of the carbonized samples by esterification: 20g of the carbonized ogbono shells were treated with 0.4g of fatty acid (stearic acid) in 200ml of n-hexane containing two drops of concentrated H₂SO₄ as catalyst. The mixture was refluxed in dean stark apparatus at 65± 2°C for 4 h. After reaction, the esterified acid–biomass was washed severally with n- hexane. The fatty biomass was oven dried at 110°C for 12h respectively (Banerjee et al., 2006). They were then kept in dry tightly closed bottle for further use.

Weight percentage gain = \( \frac{\text{Weight gain}}{\text{Original weight}} \times 100 \) (1)

Characterization of the raw and modified biomass: The surface morphology of the (raw and modified) biomass was studied using Model 302 Hitachi High Field Emission Scanning Electron Microscope and the images at 1mm and 150 magnifications. The method employed by Nwabanne and Igbokwe (2008) was adopted to carry out Fourier Transformed Infrared analysis of raw and modified biomass (Ogbono shell) using BUCK model 500 M infrared spectrophotometer. The sample was prepared using KBr and the analysis was done by scanning the sample through a wave number range of 500 to 4000 cm⁻¹. The proximate analysis parameters and the method of analysis were according to the American Society for Testing and Materials (ASTMD 5142, 3174, 872 and 3175 for moisture, ash, volatile and fixed carbon respectively) (Diadem, 2012).

Adsorption Experiment: The sorption of crude oil contaminated water was carried out following the method described by Banergee et al. (2006). Exactly 50ml of water was measured inside a 100ml beaker. A certain amount of crude oil (0.1-1.4g) depending on the oil/water ratio for a particular run was added into the beaker. The oil/water mixture was manually stirred at varying minutes to ensure proper dispersion of the oil in water. 0.2g of the modified adsorbent was weighed into the beaker. The beaker containing the sorbent, oil and water was put into a water bath at a varying temperature. The mixture was stirred for a period of time, depending on the particular run. After which the mixture was filtered through a net of approximately 250µm. The weight of the net before and after the filtration was recorded. Meanwhile, the net after the filtration was allowed to stay for 24hours before the final weight was taken.

Percentage removal was also calculated according to the equation below

\[ \% \text{ removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \] (2)

\[ q_e = \frac{(C_0 - C_e)V}{M} \] (3)

C₀=Initial oil concentration (mg/l); Cₑ=Equilibrium Concentration oil at certain time; Qₑ= Equilibrium adsorption in (mg/g); V= Volume of the aqueous mixture in cm³; M = Mass of the activated biomass (esterified ogbono shell) in (g)

RESULTS AND DISCUSSION

Proximate analysis of the raw and modified biomass: The characteristics of raw and modified biomass were shown in Table 1. From the Table, it can be seen that the raw biomass (ogbono shell) have low fixed carbon, surface area and high volatile content and as such suggest that the sample requires activation. Increase in fixed carbon and reduction in volatile matter of the activated biomass shows that activation improved the surface area of the biomass for adsorption.

As observed from table 1, the surface area of ogbono shells increased from 114cm² (raw ogbono shell) to 190.5cm²(Esterified ogbono shell) after modification with stearic acid thereby increasing the number of micropores within the surface the biomass for oil sorption and further validates the effectiveness of biomass modification by esterification and ogbono shells as a good sorbent for oil removal. Similar results on acetylated ogbono shell (199.3cm²) has been reported by Alothman et al., (2011).

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Table 1: Physical properties of the raw and modified ogbono shell

| Adsorbents         | Ash content (%) | Volatile matter (%) | Carbon content (%) | Surface area (m²/g) | pH  |
|--------------------|-----------------|---------------------|-------------------|--------------------|-----|
| Raw ogbono shell   | 7.4             | 28.6                | 56.5              | 114                | 6.9 |
| Carbonized ogbono shell | 5.7           | 21.4                | 64.2              | 129.4              | 7.1 |
| Esterified ogbono shell | 5.6           | 19.3                | 69.4              | 190.5              | 7.2 |

SEM Analysis Results: SEM Analysis is used to study the morphological compositions of the biomass before modification and after modification. There were more pore spaces in the carbonized and activated adsorbents than in the unmodified biomass. Availability of pore spaces favours adsorption process since it is a surface reaction. The surface morphologies of the raw biomass (Ogbono shells), carbonized biomass, and esterified biomass were presented as shown in fig 1 to 3. It was observed from fig 1 that the samples were internally bonded together. It can be observed from the figures that a bulk of microstructure which in turn is composed of a homogeneously distributed network comprised of small filamentous and fistulous crystallites showing the presence of minerals. In the matrix, Luminous and non-luminous features can be seen.

Fourier Transform infrared (FTIR) of the modified and unmodified biomass: Bands were assigned according to the published article (Starsinic et al., 1984; Supaluknari et al., 1998). Fourier transforms infrared spectra of the raw biomass, carbonized biomass, and esterified biomass are presented in Fig 4 to 6. The frequencies were assigned to the respective functional ground, interpreted and summarized in Table 2. From Table 2, it was observed that the biomass samples have numerous functional groups and the major functional groups present are O-H, N-H, N-CH₃, C=C-C, C-Cl, Si-O-Si. Petroxides bands stretches between 9650-1095cm⁻¹, Aromatic phosphate P-O-C stretches between 1300-1390cm⁻¹, Aromatic C-H in plane bend, Silicon oxy compounds Si-O-Si stretches between 1125-1295cm⁻¹, C-Cl stretch, alkyne C-C bend lies between 700-900cm⁻¹, hydroxyl group OH stretch was observed between

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4000-3650cm⁻¹, primary amine group NH stretches between 3200-3450cm⁻¹. Aliphatic secondary amine NH stretches between 3150-3200cm⁻¹. Normal polymetric stretch of hydroxyl group lies between 3050-3100cm⁻¹. Methylamino acids N-CH, C-H stretches between 2950-2920cm⁻¹. Cyanide ion, thiocyanate ion stretches between 2290-2550cm⁻¹. Isothiocynate –CNS bond stretches between 1600-1795cm⁻¹. Conjugated keton, open chain acids anhydrides stretches between 1600-1750cm⁻¹. The bending of the hydroxyl group was further observed at the stretch between 1450-1595cm⁻¹. Fig 4 showed that the entire spectrum had more or less similar broad characteristic absorption bands.

The bands at 1541cm⁻¹ and 1442cm⁻¹ is normally present in organic substance (biomass) with more Lignin content. The band was shifted from strong absorption to medium intensity in the spectra of stable product. This reveals the effectiveness of modification of biomass using esterification.

Batch adsorption Studies: Changing different parameters, such as pH, oil/water ratio, contact time, and temperature at constant adsorbent dosage, the adsorption capacity of the activated ogbono shell was investigated.

Effect of oil/water ratio and time: The initial concentration of oil layers within the polluted water surface determines the amount that will be absorbed into the micro pores with the surface of a given amount of adsorbent (Bhatia et al., 2007; Brandao et al., 2010). Hence the effect of oil water ratio was studied for the initial oil concentration ranging from 0.2 to 1.4g/100cm³ and the results were presented in Fig 7. The figure shows that increase in concentration of oil
on the surface of water decreases the rate of adsorption of oil by the biomass with increase in time.

### Table 2: FTIR spectrum of modified and unmodified ogbono shell

| Raw or uncarbonized ogbono shell | Carbonized or untreated ogbono shell | Esterified ogbono shell | Assignment |
|----------------------------------|--------------------------------------|-------------------------|------------|
| Frequency (cm⁻¹)                | Frequency (cm⁻¹)                      | Frequency (cm⁻¹)        | Assignment |
| 3825.517–3876.67               | 3793.298–3875.55                       | 3801.977–3876.67       | O-H stretch |
| 3675.501                        | 3627.504                              | 3684.566                | Hydroxy group, H-bonded, O-H stretch |
| -                                | 3522.591                              | 3558.035                | NH stretch |
| 3408.157                        | 3305.789                              | 3393.225                | Aliphatic secondary amine, NH stretch |
| 3275.004                        | 3182.727                              | 3165.456                |            |
| 3074.927                        | 3029.927                              | 3025.035                |            |
| 2576.209                        | 2530.146                              | 2574.765                | Methylamine, N-CH3, C-H stretch |
| 2974.846                        | 2992.879                              | 2968.398                |            |
| -                                | 2310.194                              | 2443.552                | Isoximate (-N=C=O asym. Stretch) |
| 2021.355                        | 2066.473                              | 2048.547                | Cyanoate ion, thiocyanate ion and related ions |
| 2135.567                        | 1932.828                              | 1859.351                | Isocyanate (-NCS) |
| 1857.261                        | 1839.551                              | 1866.344                | Conjugated ketone, open-chain acid anhydride |
| 1619.507                        | 1742.96                               | 1619.528                | C=C-C Aromatic ring stretch |
| -                                | 1341.907                              | -                       | O-H bend |
| 1417.846                        | -                                    | -                       | N-O asymmetric stretch |
| 1306.14                         | 1383.956                              | 1310.616                | Aromatics phosphates (P-O-C stretch) |
| -                                | 1279.721                              | 1221.848                | Aromatic C-H in plane bend, Silicon – oxy compounds, Si-O-Si |
| 867.3509                        | 827.8279                              | 842.6113                | Peroxides, C-O-O- stretch |
| 770.6973                        | -                                    | 719.3619                | C-Cl stretch, Alkyn CH-H bend |
| -                                | 698.3854                              | -                       | C-Cl stretch, Alkyn CH-H bend |

That is, there was decrease in percentage sorption as the crude oil concentration increases. This could be that the porous surfaces of biomass (adsorbents) available for the removal (adsorption) of oil were becoming saturated as the crude oil concentration increases. While the amount oil adsorbed (removed) per unit mass increased with increase in initial oil concentration, the adsorption percentage decreased, this can be explained because at lower concentration, the ratio of the initial number of the oil molecules to the available surface area is low (Arivoli et al., 2009). Because for a fixed concentration of active sites remaining the same, the number of substrate ions accommodated in the interlayer space increased so that the removed ones is decreased. This may be due to the fact that with increase in initial concentration of the oil, more oil molecules are also adsorbed on the surface of the biomass (adsorbent). Similar results were obtained by many workers such as (Cheenmatchaya and Kungwakunakorn, 2014; Cojocaru et al., 2011; Cunha et al., 2011). Initially, the highest average percentage of 75.2% oil layer was absorbed with concentration of 1.4g/100cm³ after 10 minutes but decreased progressively with increase in time. This is because the amount of oil adsorbed per unit time at the beginning of the process is significantly influenced by the initial concentration of oil (Deschamps et al., 2003).

**Effect of pH and time:** The effect of pH at 3, 5, 7, 9 and 11 and time of 10, 20, 30 40 and 50 mins is as shown in fig 8. It could be seen from fig 8 that maximum percentage removal of 96% oil layers happened at pH 5.0 after 50 minutes and decreased as the pH increased up to pH 11.0. This is because at acidic pH, the degree of protonation of the surface of the activated biomass will be more which will result in increase in diffusion...
and subsequently increase in oil removal (adsorption) due to electrostatic attraction (Ladhe et al, 2011; Pragnesh et al, 2011). The decreases in percentage removal of oil from pH 7 and above could be also due to the fact that oils are prototypical apolar solvents. Also, this could be due to the number of positively charged adsorbent sites decreasing as the pH increased. This causes the number of negatively charged surface sites to increase which did not favor the adsorption of negatively charged oil cations due to electrostatic repulsion. This agrees with the report by Bansal et al., (2011) which state that oil is non-polar as it consists of non-polar bonds which repels atoms having similar electro negativities and with net dipole.

**Conclusion:** Analysis of data in this investigation showed that carbonized ogbono shell modified by esterification with steric acid can be used as economic, effective and eco-friendly adsorbents for the maximum removal of crude oil from water surface. FTIR analysis of activated and uncarbonized biomass (ogbono shell) shows that they consist mainly of organic compounds such as hydroxyl group, amino group, amine and conjugated ketones.

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