Comparative Analysis and Regenerative Studies of Alkaline Modified Groundnut Shell as Adsorbent for the Removal of Oil Layer from Polluted Water

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Authors’ contributions

This work was carried out in collaboration between both authors. Author OSE designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors OSE and NHO managed the analyses of the study. Author NHO managed the literature searches. The authors read and approved the final manuscript.

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ABSTRACT

This work focuses on the comparative analysis and regenerative studies of alkaline modified groundnut shell as adsorbent for the removal of oil layer from water surface. The groundnut shell was carbonized at 800°C before chemical activation. Scanning Electron Microscope (SEM) and UV/VIS Spectrophotometer were used in characterizing the adsorbents. Batch adsorption studies were carried out to determine the effect of process conditions on the percentage removal. Regeneration studies was applied to investigate the reusability of the adsorbent after each batch of experiments. SEM characterization revealed that micro porous space on the surface of the adsorbent (groundnut shell) increased significantly after activation. The surface area of the composite increased from 28.5 cm² to 87.9 cm² after activation. pH of point zero charge ranging from -1.41 to -3.56 revealed negative charge predominance on the surface of the adsorbents and adsorption was found to be very fast at low pH due to strong electrostatic force between oil layer and ion diffusion on the adsorbent surface. The optimum adsorption time was found to be

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100 minutes with 79.4% oil removal at pH of 6.9. Regeneration of the adsorbent after each batch of experiments shows that the surface area remained intact at 77.8 cm$^2$ which is almost equal to the modified (unused) adsorbent. Experiments with the regenerated adsorbent shows that 84.89% of oil was removed at oil water ratio of 0.2 g/100 cm$^3$ against 88.56% of oil removed using the modified adsorbent at the same oil water ratio. Thus, the sorption process was feasible, spontaneous, rapid and showed high performance with a proven ability of the adsorbent to be regenerated after use. However, the present approach has the advantage of simplicity, less time consuming and most importantly, low cost considering the availability of groundnut shell at no cost.

Keywords: Adsorption; groundnut shell; crude oil layer; regeneration.

1. INTRODUCTION

Studying adsorption capability of various agricultural materials as good adsorbents is an interesting and continuously expanding field of study. The use of agricultural adsorbents seems to have been recognized as an effective and remarkable control measure in many oil spill situations [1]. For many years, crude oil spill and its alarming pollution have been a big problem in the issues that concerns environment over the world and in particular the oil rich Niger Delta of Nigeria [2]. One of the main sources of water pollution is crude oil spill. Oil and petroleum products such as diesel, gasoline, AGO etc., can destroy and pollute sources of water such as seas, or underground waters. Oil spills over the oceans and seas requires urgent attentions due to their environmental and economic importance. [3, 4]. In aquatic field; different aquatic species have different sensitivity to crude oil/crude oil products pollution in water. However, the crude oil spill 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, thereby causing starvation to lives living under the water [2, 5]. Leakages from underground storage tanks, petroleum products trucks accidents, pipelines vandalism and other many ways of crude oil distribution systems have become the most commonly detected source of underground and surface water pollutants [2, 6]. In view of the aforementioned, there has been a tremendous attention regarding the treatment of water and wastewater in recent years. Generally, the conventional method of water and wastewater treatment technologies including flocculation, ultrafiltration, biological treatment and coagulation [7-9] do not seem to be economically viable [2, 10]. This research therefore has the potential of developing an alternative source of adsorbent from biomass for water treatment. The 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 readily available at no cost, naturally occurring, stable and require minimum care or maintenance [10]. Therefore, this study intends to study the modification of these agricultural wastes via heat and chemical treatment, thereby making it suitable to be used as adsorbents for remediation of contaminated water.

2. MATERIALS AND METHODS

2.1 Materials Sourcing and Conditioning

The groundnut shell used in this work was obtained from Nkpologu in Uzo Uwani LGA of Enugu State. The crude oil sample was obtained from Agip oil field in Omoku, Rivers State Nigeria. The biomass was oven dried at 105°C. The other materials used in the experimental work include the followings: distilled water, (analytical grade), Potassium hydroxide (KOH), $\text{H}_2\text{SO}_4$, HCl, sieving net, stearic acid, n-hexane. They were all purchased from a chemical shop at Ogbete main market Enugu Nigeria and they were of analytic grade and was used without further purification.

2.2 Carbonization of the Biomass

The biomass was washed with water to remove unwanted materials and oven dried at 105°C for 2hrs. The dried biomass was carbonized in a muffle furnace at 600°C for 8 hours respectively. After the carbonization, the samples were left to cooled and stored in a dry transparent container for further use [11].

2.3 Modification of Carbonized Sample with Alkaline

Modification was done using the method according to Basta et al. [12], samples of carbonized biomass were impregnated with 4 ml of 3 molar KOH, stirred to form paste and left for 2 hours, respectively. The samples were
decanted and transferred to an oven at 110°C for 7hrs. The dried samples were later removed from the oven, washed with 0.1molar HCl and rinsed with hot distilled water to attain neutrality of 7. The samples were decanted and returned to the oven at 110°C for 24hrs to dry properly and thereafter was transferred to the muffle furnace and further carbonized at 800°C for 1hr. the modified sorbents were kept in tightly closed bottles for further use.

2.4 pH of Point Zero Charge (PZC)

The salt addition technique was performed according to Usman et al. [13]. In a series of 100-ml centrifuge tubes 0.2 g of each of the biomass was added to 50-ml of 0.1 mol/dm³ NaCl solution. The pH was adjusted with 0.1 mol/dm³ HCl and 0.1 mol/dm³ NaOH as required get the appropriate pH range of 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11. The pH values of the supernatant in each tube were denoted as pHᵢ. The samples were shaken for 24 h using a rotary agitator (Wrist-Action Shaker, Cole Parmer 51704 Series) at 200 rpm. After settling, the pH values of the supernatant in each tube were measured and denoted as pHᵢ. The PZC was obtained from the plot of ΔpH (=pHᵢ – pHᵢ) against pHᵢ. Experiments were repeated with a 0.05mol/dm³ NaCl solution. Each set of experiments was performed in triplicate and the mean value was taken.

2.5 Batch Adsorption Experiment

The adsorption study was carried out in batch experiments. Five sets of constant initial concentration of 10g/l of crude oil-water mixture were prepared. Onto the floating crude oil, different weights of adsorbents such as 0.2g, 0.4g, 0.6g, 0.8g and 1.0g was added and filtered after 60mins at ambient temperature and constant pH of 7 with a sieving net, they were air dried overnight and weighed. The process was repeated by increasing their concentration progressively from 10g/l to 50g/l. The amount of equilibrium adsorption (qe) and percentage removal was evaluated using equation 1 and 2 respectively;

\[ qe = \frac{(Co-Ce)}{w}V \]  \hspace{1cm} (1)

Percentage of oil removed was also calculated according to the equation below

\[ \% \text{removal} = \frac{(Co-Ce)}{Co} \times 100 \]  \hspace{1cm} (2)

Where;

- \( Co \) = Initial oil concentration (Mg/l)
- \( C_t \) = Concentration lead at time t (20, 40, 60, 80 and 100 mins)
- \( V \) = Volume of the solution (ml)
- \( w \) = Mass of the adsorbent (activated biomass)

2.6 Characterization of the Biomass Wastes

The biomass wastes were first characterized by carrying out proximate analysis and thereafter, instrumental analysis using Scanning Electron Microscopy (SEM). 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) [14-16]. The surface area of the adsorbents was determined according to method described by Al-Qodah and Shawabkah [17].

2.7 Regeneration (Reusability)

The regeneration of the oil laden sorbent was carried out following the method described by Chen et al. [18] with some modifications. The oil laden sorbent was weighed and put into a porcelain crucible. The crucible was introduced into a muffle furnace and the temperature was set at 300°C. At this temperature, the adsorbed oil was burnt off leaving the regenerated sorbent. The burning lasted for 5hours after which the furnace was allowed to cool overnight before the sorbent was removed. The regenerated sorbent was characterized by proximate analysis. The effect of time on the adsorption of crude oil using the carbonized and modified biomass was investigated. Five sets of initial concentration of crude oil-water mixture were prepared by mixing 0.2 g of crude oil in 100 ml of water. Onto the floating crude oil, a constant weight of 0.1g of the modified and regenerated biomass were added separately at a varied time interval of 10 mins, 20 mins, 30 mins, 40 mins and 50 mins at a pH of 7 and ambient temperature. The percentage of oil adsorbed was evaluated thereafter. The experiment was repeated for oil water ratio by keeping other factors constant.

3. RESULTS AND DISCUSSION

3.1 The Proximate Analysis Results

The proximate composition of groundnut shell was carried out and the results are given in Table
1. The biomass was mainly composed of volatile matters before carbonization and further modification with fixed carbon content of 15.2% with a very low surface of 28.5 cm². It was observed that carbonization reduced the volatile content of the groundnut shell significantly and increased the fixed carbon and surface area. This concurred with the report by Ilaboya et al. [19] that carbonization removes the volatile component of organic wastes and increases the number of micro-pores within the surface. Surface area of the biomass was significantly increased from 28.5 to 87.9 cm² and hence a greater potential adsorbent for crude oil removal. The result is above the surface area of 76.4 cm³ reported by Ilaboya et al. [19] for alkaline activated groundnut shell.

3.2 SEM Observation of the Unmodified and Modified Groundnut Shell

Fig. 1 represents the SEM image of the raw groundnut shell at different magnifications. It can be observed from the figure that a bulk of microstructure which in turn is comprised of a homogenously distributed network comprised of small filamentous and fistulous crystallites showing the presence of minerals. The matrix shows both luminous and non-luminous features which indicated the presence of minerals distributed in the organic matrix and as surface coverage. Features such as cracks, veins, fissures and cleats can be seen. The bright luminosity indicates the presence of aluminum, silicon, calcium (lithophytes) and iron (siderophile), the dark luminosity indicates the presence of chalcophiles like lead, manganese, chromium, cadmium, zinc etc. some layers, Islands and hills and valleys can be seen randomly distributed throughout the micrograph which are as a result of calcinations of CaMg(CO₃)₂ (dolomite) and CaCO₃ (calcites) some discrete and coherent crystals of irregular shapes represent the presence of iron. It is inferred that the groundnut shell sample under study contains large proportions of silica, calcium, carbonate, iron oxide, aluminum and some proportions of elements such as manganese, potassium and other trace metals such as lead, chromium, copper etc that proved to be in agreement with other previous work. To increase the void spaces and hence the adsorption capacity of the groundnut shell, thermal activation and modification with alkaline were characterized. The mineralogical studies of the two activation methods of groundnut shell were done.

The SEM image of the two samples were provided in Figs. 2 and 3. In the two samples, it can be seen that numerous aggregated particles can be seen. The porosity of the two samples increased relatively to the raw samples (Fig. 1) and this provides strong evidence that significant number of solid particles (inorganic elements) had been removed. However, the surface coverage is still bright and luminous indicating the presence of mineral phase. It can also be seen that the porosity of the alkaline modified sample (Fig. 3) has more volume than the unmodified sample. The least in the samples is unmodified which proved that modification with alkaline increases the porosity of the carbonized groundnut shell. These can be attributed to the fact that this chemical reacts with inorganic solid particles in the porous spaces thereby creating more void volume.

The SEM micrograph of the two samples provided in Figs. 2 and 3 respectively caused morphological changes in the particles and did enormous harm to the surface by removing some of the inorganic elements. However, alkaline modified sample seems to be effective in the adsorption experiment.

3.3 Batch Adsorption Study

Batch adsorption method was employed by varying different parameters such as crude oil concentration, contact time and pH using alkaline modified carbonized groundnut shell to find the best suited conditions for the removal of crude oil from water surface. The results of adsorption studies are shown in Figs 4, 5 and 8.

3.4 Effect of Time

The effect of time on adsorption capacity and percentage removal of oil by unmodified and alkaline activated groundnut shell are shown in Fig. 4. Both the percentage removal and the adsorption capacities increased with increase in time until equilibrium was achieved. It was observed from Fig. 4, that the optimum adsorption/removal of oil with alkaline activated groundnut shell occurred at a time of 100 mins with 79.42% of oil adsorbed. The percentage remained the same even at the time beyond 100 mins, which indicates that the adsorption has reached equilibrium. From figure also, the optimum adsorption/removal of oil with unmodified groundnut shell adsorbents occurred at 100 mins with 71.72% removal. The difference
in percentage removal was occasioned by the formation of monolayer on the surface of the adsorbents, thus the extent of removal of oil layer from the solution was then controlled by the rate of transport of the adsorbate species from the outer layer (pore sites) to the inner layer sites of the adsorbents, hence adsorbent with more microporous pores removes greater percentage of oil layer (adsorbate) according to Okpe et al. [20]; Asadu et al. [16]; Nwabanne et al. [21]; Nwabanne et al. [22]. It can be seen that the two adsorbents have demonstrated a good potential for the adsorption of oil from solution with alkaline activated groundnut shell showing a greater potential as shown in Fig. 4. 67.6% removal of oil layer by alkaline activated groundnut shell has been reported by Nwabanne et al. [22] while 76.93% removal was reported by El-Kafrawy et al. [23]. Adsorption of oil layer onto cassava peel composite reached equilibrium at a relatively lesser time (100 mins) compared to others, indicating high kinetic performance. This observation agrees with the report by Dumitru and Laura [24].

Table 1. The proximate composition of groundnut shell

| Adsorbents         | Groundnut shell (GS) |
|--------------------|-----------------------|
|                    | Raw                   | Carbonized            | Alkaline modified |
| Fixed carbon (%)   | 15.2                  | 37.8                  | 49.4              |
| Volatile matter (%)| 64.8                  | 51.6                  | 19.9              |
| Ash Content (%)    | 2.0                   | 4.6                   | 7.4               |
| Surface area (Cm²) | 28.5                  | 26.7                  | 87.9              |
| Moisture content 9%| 8                     | 4.2                   | 3.3               |

Fig. 1. SEM image of raw groundnut shell at different magnifications

Fig. 2. SEM image of carbonized groundnut shell at different magnifications
Fig. 3. SEM image of alkaline activated groundnut shell at different magnifications

Fig. 4. Effect of time on adsorption of oil layer unto modified and unmodified groundnut shell

3.5 Effect of Crude Oil Concentration

From Fig. 5, it can be clearly seen that the removal efficiency of the crude oil with the alkaline modified groundnut shell samples increases with increase in oil concentration. This shows that alkaline modification of groundnut shell is very effective for removal of crude oil spills at higher concentration of oil. This is in accordance with the results of other literature. As the oil concentration increases, the removal efficiency/capacity increases relatively to non-modified groundnut shell. This is as a result of larger void space (porosity) created by those modifying agent which trap more oil in the void spaces.

Fig. 5. Effect of crude oil concentration on the sorption of oil layer unto modified and unmodified groundnut shell
3.6 Effect of pH

3.6.1 pH of point zero charge

The pH of point zero charge (PZC) was evaluated for untreated and treated groundnut shell. The results are expressed at both ionic strengths (0.05 and 0.1 mol/dm$^3$) and point zero charge was clearly identified as shown in Figs 6 and 7. It was observed that the point of zero charge (pzc) where ranged between 5.36±0.1 and 9.56±0.1 which is evident that the surfaces of the biomass (adsorbents) were predominantly negatively charged and gives a clear indication that for the maximum removal of the adsorbate (oil layers), the pH of the adsorbent need to be adjusted to serve the purpose. It was observed that the pzc decreased with increase in ionic strength. Similar results were reported in literature by Naema et al. [25].

3.7 Percentage Removal by the Adsorbents at Adjusted pH

The effect of pH on the percentage removal of the adsorbate (oil layer) by the activated biomass was carried out as shown in Fig. 8. The highest adsorption capacities were recorded between the pH of 5.0 and 6.9 for both the modified and unmodified groundnut shell. Highest percentage removal was recorded at pH 6.7. The adsorption capacity and percentage adsorption increased gradually from acidic region to alkaline region but decreases as the pH moved above 6.9. This buttressed the earlier results as indicated from pH of point zero charge (pzc) showing that the surface of the adsorbent is predominantly negative. At high acidic region the adsorption capacities were low and can be compared with the values at towards alkaline region. It can be seen that the optimum pH for the adsorption of oil layer by the adsorbents lies at pH 6.9. The sharp decrease in percentage adsorption after pH 6.9 could be attributed to saturation of the adsorbent at equilibrium region. The pH effect can be likened to temperature effects on the rate of removal of oil by altering the molecular interactions (affinity) and solubility of the adsorbates which is in agreement with the reports by Md-Awual et al.[26], that the adsorption of adsorbate (oil layer) onto the adsorbents is at optimum due to high affinity of the layers to the microporous space which increases adsorption capacity especially when there are no competing ions.

3.8 Regeneration studies (Reusability)

Physical characterization of the regenerated adsorbent.

The physical properties of the regenerated adsorbents in comparison with modified adsorbents were given in Table 2. The regeneration method adopted was thermal treatments. It was observed from Table 2 that the surface area of regenerated groundnut shell was 77.8 cm$^2$ which was very close to the surface area of 87.9 cm$^2$ of the unused alkaline modified groundnut shell. It was also discovered from Table 2 that the pH of the regenerated biomass increases thereby making the surface of adsorbent more alkaline. The behavior of the biomass after recovery was similar to the report by Didem, 2012, who reported the surface of regenerated alkaline activated corn silk to be 118.7cm$^2$ against the surface area of 126cm$^2$ of modified alkaline (unused) corn silk. Observations from Table 2 are evident that the adsorbents can be regenerated for further use.
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Fig. 7. The point of zero charge for alkaline modified groundnut shell @0.05 and 0.1mol/dm³

Fig. 8. Effect of pH on oil removal onto modified and unmodified groundnut shell

Table 2. Physical properties of the activated and regenerated adsorbent

|                        | Modified groundnut shell | Regenerated groundnut shell |
|------------------------|--------------------------|-----------------------------|
| Ash content (%)        | 7.4                      | 6.3                         |
| Volatile matter (%)    | 19.4                     | 18.9                        |
| Carbon content (%)     | 49.4                     | 23.9                        |
| Surface area (m²/g)    | 87.9                     | 77.8                        |
| pH                     | 7.1                      | 7.6                         |

3.9 Effect of Time

Fig. 9 demonstrated the effect of time on sorption of oil onto regenerated biomass. It was observed from Fig. 9 that the trends are the same for both the modified (unused) groundnut shell and regenerated groundnut shell i.e., increase in time, increases the rate of oil sorption by the biomass. Furthermore, there was a close relation between the percentage oil sorption between the regenerated biomass and the unused biomass taking into consideration the amount oil removed by both biomass at a given time. It was also observed from Fig. 9, that maximum percentage of oil was removed by both regenerated and modified biomass happened within 30 minutes of the sorption experiments. This could be attributed to the fact that oil gets trapped very fast within the pores on the surface of the adsorbents and the faster the oil is trapped, the less likely it will be dispersed and get away further into the water surface.
3.10 Effect of Oil Water Ratio

The effect of oil water ratio on the sorption of oil onto regenerated biomass followed a similar trend. The effects were studied for both the modified and regenerated biomass using oil to water ratio between 0.2g/100cm$^3$ to 1.0g/100cm$^3$ at a constant adsorbent dosage of 0.1g. The results were presented as shown in Fig. 10. It was observed that the floating oil was removed as soon as the biomass was added but the percentage removal of oil by both regenerated and modified biomass decreased with increase in concentration of oil. The percentage of oil layer removed at 0.2g/100cm$^3$ by the modified biomass was 88.56% while it was 84.89% for the regenerated biomass. The closeness in the percentage removal at the same oil water ratio by the biomass is a clear prove that the used adsorbent produced using groundnut shell can be regenerated after used for further application.

4. CONCLUSION

The activated biomass groundnut shell demonstrated a good potential as an adsorbent for the remediation of crude oil contaminated water as observed from the batch adsorption studies. Characterization of the biomass wastes with scanning electron microscope (SEM) after carbonization and chemical treatments also revealed that the number of micro porous surface of the adsorbents increased significantly. The sorption of oil by the alkaline activated groundnut shell attained equilibrium after 100minutes with
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Competing interests
Authors have declared that no competing interests exist.

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