Using Spectroscopy for Oil Sorption Analysis and the Development of Biodegradable Sorbent from Bambara Nut Husks

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ABSTRACT

Developing measures to cleanup oil spillage in water is a serious concern for researchers due to the environmental damages associated with oil spillage. There are many ways that oil spillage can be tackled, but sorption has proven to be promising, and a lot of experiment has been targeted towards increasing the efficiency and the environmental friendliness of sorption. However, a serious challenge that is often encountered in sorption experiment is the inadequacy and the complications of the gravimetric method that is often applied. This work, therefore, concentrated on developing a standard method based on spectroscopy of oil concentration and absorbance, as an alternative to gravimetric analysis, which would provide accurate sorption analysis results without a combination with other instrument. A standard equation of concentration and absorbance was developed, and the regression coefficient at 410nm was 0.9909, which was close enough to 1.0, making spectroscopy an accurate and simple method of sorption analysis. Secondly, bambara nut (Vigna subterrancea) husks were modified by acatylation and applied as crude oil sorbents. The result indicated that acetylation of the husks replaced the short chain hydroxyl group with long chain alkyl groups and increased the hydrophobic nature of the husks, thus enhancing the sorption capacity. The effects of time on the sorption capacity of the modified husks were studied and the result shows that within 6 minutes, the modified husks can absorb up to 3.5g of oil per gram of the sorbent as compared to the maximum of 3.0g/g obtained with the un-modified husks. The effects of sorbent dosage on the sorption capacity of the husks were equally studied and the result indicated that low dosage of 0.05g per 20 ml of oil/water mixture at a concentration of 0.02g/mL gave high sorption capacity of 5g/g and high dosage of 0.25g/20 ml gave low sorption capacity of 1.5g/g. Conversely, low dosage gave percentage removal and high dosage gave high percentage removal. Equally, study on the effects of oil concentration on sorption capacity showed that high oil concentration of 0.06g/mL could result to high sorption capacity of 6.0g/g while low sorption capacity of 1.0g/g can could result from low oil concentration of 0.01g/ml.

Index Terms: Visible spectroscopy, sorbent, sorption, process parameters

1 INTRODUCTION

Oil spillage, mainly due to human mistakes during oil drilling operations and storage, is an environmental issue that has necessitated the development of materials for effective cleanup. There is a widespread use of chemical dispersants to treat oil spills, but the toxic products of such reaction emanating from the use of harmful chemicals fail to balance life in the ecosystem [1]. Treatment of oil spillage by sorption earns its popularity for their simplicity, affordability and effectiveness [2]. Traditionally, companies have applied synthetic organic materials such as polypropylene, and polyurethane in commercial supply, which is good for their oleophilic-hydrophobic properties, but the drawbacks stems from their non-biodegradability [3]. In addition, some expensive inorganic materials like vermiculite, perlite, and clay are equally in use, though they are ineffective for their low buoyancy [1]. Due to their biodegradability and availability, agricultural residues have drawn the recent attention as oil sorbents. Some organic natural wool have shown to have higher sorption capacity than some synthetic sorbents [4]. Possibly, due to the waxy nature of some fibers like Kapok, they have shown higher sorption capacity than synthetic substances like polypropylene [5].

However, the presence of hydroxyl group (OH) in cellulose, hemicelluloses and lignin components of agricultural residues attracts both water and oil, making the sorbent to sink in water [6]. Barros et al. [7] reported that

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agricultural sorbents could absorb up to 0.39 g of oil per gram of sorbent, but the challenge was how to deal with the difficulty of sorbent sinking after adsorption. In order to improve the sorption capacities of agricultural residues, the OH group that makes the biomass to sink cab be replaced with carboxylic group in the process of esterification. In other words, agricultural lignocellulosic residues are hydrophilic, requiring treatments to improve the sorption capacity of the substrates[8]. Banerjee et al. [2] modified the sorbent capacity of biomass by treating sawdust with fatty acid (oleic, stearic and decanlic acid) in n-hexane with sulfuric acid as the catalyst. The presence of strong FTIR band at 1735 cm-1 and 1235 cm-1, replacing strong bands at 2356 cm-1 and 1635 cm-1, shows that cell –OH has been replaced by a long chain alkyl group, cell- OCOC17H33, which has high oil/water selectivity, during the esterification process. Similarly, Pei-Shi et al. [9] modified expanded perlite with stearic acid and reported a maximum sorption capacity of 46, which was 191 times higher than that of the unmodified perlite. Yusof et al. [1] modified the sorption capacity of coconut coir by esterification with long chain fatty acid chloride, oleoyl chloride, and short chain fatty acid chloride, octonoate chloride, and reported that high sorption capacity is associated with long chain alkyl groups in the sorbent.

Aside esterification, sorbents can be modified by acetylation where the sorbent is treated with acetic anhydride in the presence of N-bromosucinimide (NBS) as catalyst. Behnood et al. [6] compared the oil sorption ability of raw and acetylated bagasse and reported that acetylation could increase sorption by about 90 % with a maximum oil sorption capacity of 11.3 g/g. Likewise, Asadpour et al. [3] used acetylated corn silk to achieve sorption of 11.45 % weight gain. In addition, Lv et al. [10] modified cellulose fiber with acetic anhydride in the presence of NBS and achieved sorption capacity of about 22g/g. Therefore, chemical modifications of agricultural wastes tend to provides sorbents suitable for oil spillage cleanup.

Nonetheless, most of the experimental observations were based on gravimetric method, which hardly provides reliable and consistent results [11]. Rajakovic et al. [4] reported that gravimetric analysis alone does not provide precise results in oil sorption experiment, so it must be combined with Fourier Transform Infrared (FTIR) spectrophotometry in order to obtain reliable data. However, Evdokimov & Losev[12] stated that UV-spectroscopy has high potential in analyzing crude oil concentration. Ultraviolet- (UV-Vis) spectroscopy is applicable to crude oil analysis because many active sites in crude oil are able to form species in the UV-Vis spectrum [13]. In order to explore the usefulness of UV-Vis spectroscopy, this work focused on the development of a standard graph of crude oil concentration against the absorbance of the oil at peak wavelength. Moreover, an agricultural solid waste, bambara nut (Vigna subterrancea) husks were modified by acetylation and applied as sorbent, in a batch experiment, to determine the sorption capacity of the husks.

2 MATERIALS AND METHOD

2.1 The Crude Oil

The crude oil sample was obtained from Oando Oil Company at Port Harcourt, Nigeria. The specific gravity of the oil was 0.86 at 16°C.

2.2 The Development of Standard Graph

Different concentrations of the oil in N-hexane (0, 0.01, 0.02, 0.03, 0.04 and 0.05 g/mL) were prepared in different beakers. The absorbance of each of the mixture at a maximum wavelength of 410nm was recorded, and the graph of the oil concentration against the absorbance was plotted. The regression equation was obtained using MS Excel, and the equation was applied in calculating the relationship between oil concentration and absorbance at wavelength of 410nm during the entire experiment.

2.3 The Sorbent

The husks of bambara nut (Vigna subterrancea) were collected from Oye Market at Emene in Enugu, Nigeria.

After washing the husks with distilled water to remove sands and stones, the husks were air-dried for 2 days. Thereafter, the husks were blended and sieved with 250nm mesh, washed with distilled water and dried at 65°C for 24hours. After cooling, the husks were collected in an air-tight plastic container labeled "Un- Activated Bambara Husks (UBH).

2.4 Activation of the Sorbent

Acetylation method as described by Behnood et al. [6] was adopted in this study. From the UBH, 20g was weighed into a 500mL conical flask and 300mL of acetic anhydride was added into the flask. 0.6g of N-bromosucinimide (NBS) was equally added as catalyst. The contents were mixed thoroughly and the flask was connected to a reflux setup. After refluxing for 3hrs, the residual husks were washed with ethanol and acetone to remove any entrained liquid and by-products. The acelylated husks were dried in oven at 65°C for 24hours. After cooling, the treated husks were collected in another air-tight container labeled Activated Bambara Husks (ABH).

2.5 The Effects of Process Parameters on the Sorption of Crude Oil using UBH and ABH

The sorption capacity of the husks were determined at different sorption time, dosage of sorbent and oil concentration. To determine the effect of sorption time, 10mL of 0.02g/mL of oil in N-hexane was added into different beakers (50mL). 0.1g of both UBH and ABH was added to each of the flasks and the flasks were connected to an electro-mechanical shaker. After the first 10minutes, the first set containing both UBH and ABH were sieved using 100nm cloth mesh. The absorbance of the filtrate was recorded, and the process was repeated after the next 10minutes, and so on, until after 60 minutes. For the effects of dosage, 10mL of 0.02g/mL of the crude oil was added into different beakers. Different weight of both UBH and ABH (0.05, 0.1, 0.15, 0.2 and 0.25g) was added into each of the flasks. The flasks were connected to the shaker, and after 20minutes, the contents of the beakers were sieved and the absorbance of the filtrates were recorded. For the effects of oil concentration, different concentrations, in a set of two, of the oil in N-hexane were prepared in different beakers (0.01, 0.025, 0.035, 0.05 and 0.065g/mL). To each set of the beakers was added 0.1g of UBH and ABH, and the beakers were connected to a shaker for 20minutes. After which, the contents were filtered and the absorbance was recorded.

2.6 Calculating the Sorption Capacity

The sorption capacity was calculated using Equation 1.

$$q_t = \frac{C_o - C_e}{M} \times V \qquad (1)$$

Where

qt = sorption capacity, $^{\text{g of oil}}/_{\text{g of sorbent}}$

V = volume ofoil − hexane mixture,

M = mass of the sorbent (g),

C_o = Initial Concentration, $^{\text{g of oil}}/_{\text{mL of Hexane}}$

C_e = Final Concentration, $^{\text{g of oil}}/_{\text{mL of Hexane}}$

3 RESULTS AND DISCUSSIONS

3.1 The Crude Oil Concentration/Absorbance Standard Graph

The standard graph of concentration against absorbance of crude oil at a wavelength of 410 nm is shown in Figure 1. The coefficient of determination, R2, shows that only 0.81% of the data was not explained by the regression equation. Therefore, the equation is an adequate relationship of oil concentration and the absorbance at 410nm.

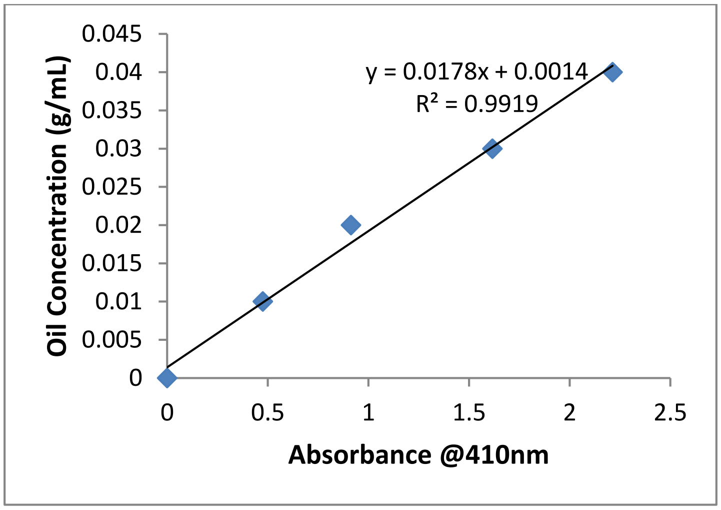

Fig. 1: The Crude Oil Concentration Standard Graph

3.2 The Effects of time of sorption capacity

The sorption capacity of ABH increased from 2.7g/g at 3 minutes to 3.4g/g at 12 minutes, and thereafter stays constant. On the other hand, the sorption capacity of UBH increased from 2.6g/g to 3.0g/g at the same time interval. Figure 2 shows the relationship between time variation and sorption capacity. This result shows that about 90% of the total sorption took place within 6minutes, which suggests that the oil trapped into the sorbent very quickly. The quick sorption means that when the sorbent is applied in open sea for oil spillage cleanup, it will not disperse so quickly, thus making the sorbents useful in practical applications [2]. The small difference in oil sorption with respect to change in time is also an indication that the sorbent displayed a fast desorption [1].

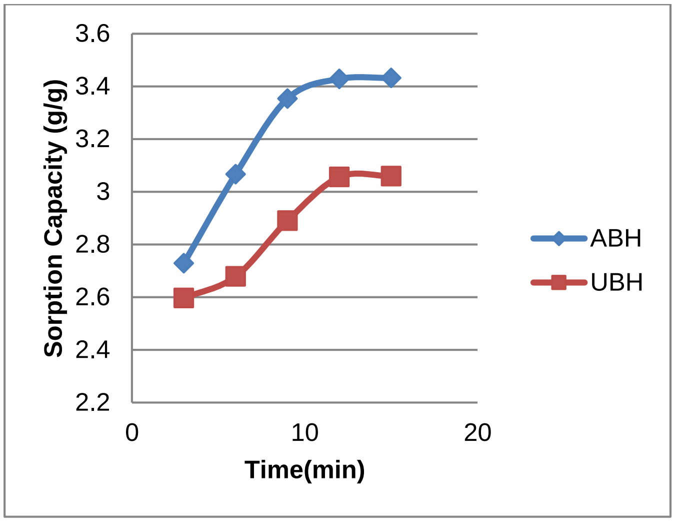

Fig. 2: The Effects of Time on Sorption Capacity

3.3 The effects of dosage of sorbent

Figure 3 shows the effect of sorbent dosage on the sorption capacity. The maximum sorption capacity of 5.0 g/g was obtained from the activated husks using a dosage of 0.05g, while the lowest of 1.3g/g was obtained with the dosage of 0.25g. At the same dosage of 0.05g, the un-activated husk gave a sorption capacity of 3.5g/g. Therefore, the activation gave rise to about 42% higher in sorption capacity, but the sorption capacity decreased with the increase in dosage. Moreover, at a dosage of 0.1g and above, the sorption capacity of both the activated and un-activated husks were the same. Conversely, the percentage removal of oil increased with the dosage as can be seen in Figure 4. At a dosage of 0.25g, about 75% of the oil was removed. This can be compared with the result obtained by Yusof et al. [1] who used activated coir to achieve 100% removal at a dosage of 0.6g. The choice of dosage to be applied in practical then depends on availability of the sorbent. Since the bambara husks are renewable and readily available, higher dosage should be applied in order to achieve high oil cleanup.

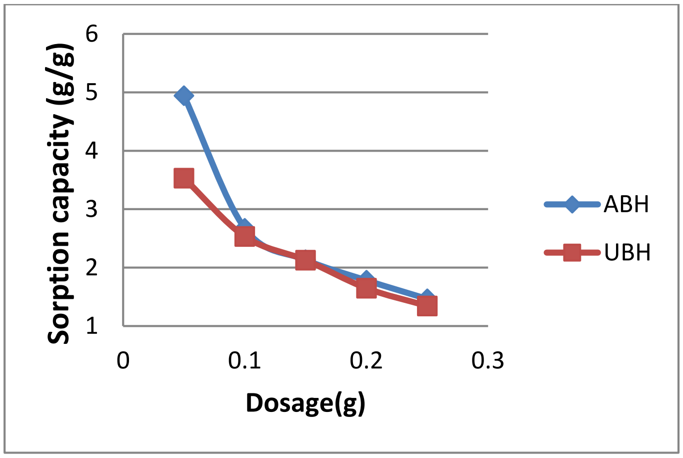

Fig. 3: The Effects of Sorbent Dosage on Sorption Capacity

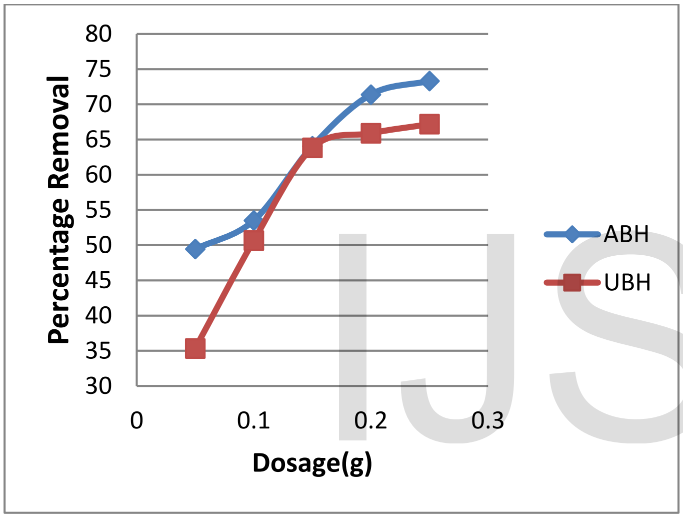

Fig. 4: The Effect of Dosage on Percentage Removal of Oil

3.4 The Effects of Oil Concentration on Sorption Capacity

The concentration of the crude oil affected the sorption capacity of the sorbents as can be seen in Figure 5. Between the concentration of 0.01g/mL and 0.06g/mL, the sorption capacity increased from 1.0g/g to 6g/g. The rate of the increase in sorption capacity, however, became almost zero when the initial oil concentration exceeded 0.06g/g. On the other hand, the sorption capacity of the un-modified husks increased from 0.9 to 3.9g/g at the same concentration range. In other words, the influence of the modification was more noticeable at high initial oil concentration. This relationship between the initial oil concentration and the sorption capacity shows that the active sites on the sorbents get saturated when the sorption capacity became constant [1]. Similarly, the percentage removal of oil reached a peak of 65% and 44% between oil concentration of 0.02 and 0.03g/mL for modifies and un-modified husks respectively.

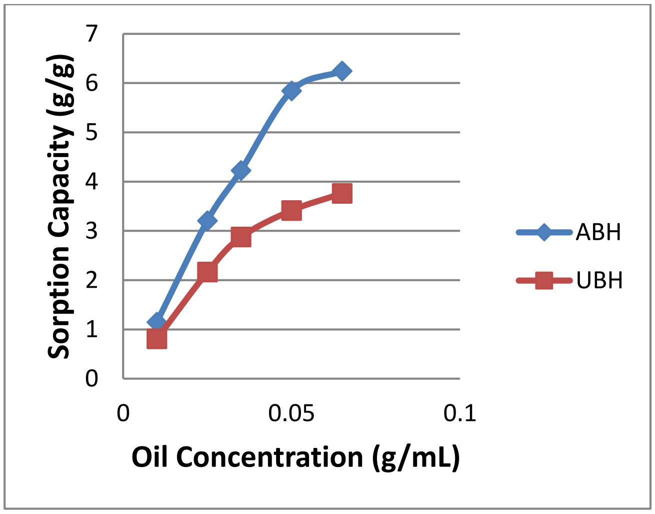

Figure 5: The Effects of Oil Concentration on Sorption Capacity

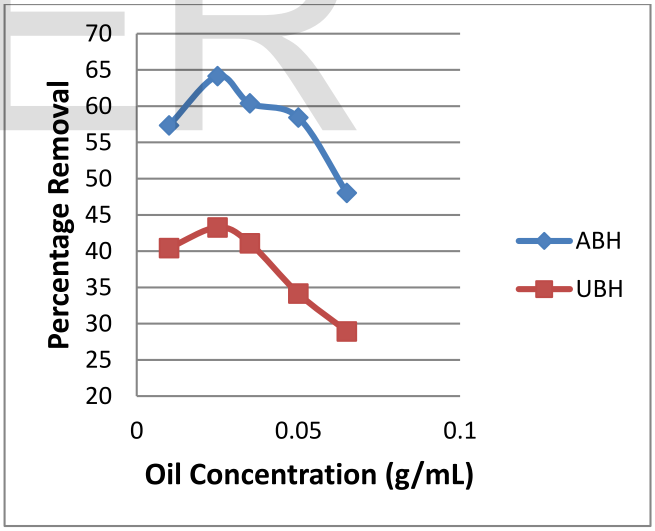

Figure 6: The Effects of Oil Concentration on Percentage Removal of Oil

4 CONCLUSION

The high coefficient of determination, R2, obtained from the plot of crude oil concentration and absorbance shows that UV- spectroscopy was a perfect tool in analyzing the sorption of crude oil. Therefore, the complications of gravimetric analysis in sorption experiment can be avoided by applying the spectroscopic method. In addition, the spectroscopic method provides adequate analysis that does not need to be combined with additional instrument, thus reducing the overall cost of the experiment. Secondly, bambara nut husks were good sorbent of crude oil and could give high sorption capacity comparable to most commercial sorbents; however, the husks had to be modified to increase the hydrophobic structure of the biomass. Furthermore, the high sorption capacity obtained with the modified husks indicates that acetylation of the husks replaced the short chain hydroxyl groups with long chain alkyl groups, thereby increasing the buoyancy of the husks. Consequently, modified bambara husks are good sorbent for oil spillage cleanup; besides, the sorption of oil with the husks takes place quickly, which means that the sorbents would not disperse easily in open water. While applying the husks for cleanup of oil spillage, the dosage should be considered because low dosage gave high sorption capacity and low percentage removal, but the reverse was the case with high dosage. It is also important to consider the concentration of the oil where the husks would be applied. As the concentration was high, the sorption capacity was high, whereas the concentration of the oil was inversely related to the percentage removal.

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