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Diesel oil sorption potential of sugarcane bagasse incorporated with human hair

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Abstract

Sorbents remove pollutants by absorption, adsorption, or both. Sugarcane Bagasse (SCB) has excellent sorption ability, but it can acquire water in its pores, limiting its field application in oil spills. Due to the high oleophilic and hydrophobic properties of human hair (HH), the study aimed to determine the sorption percentages of SCB incorporated with HH of varying ratios in diesel oil. Three treatments with the ratios (1:1), (1:3), and (3:1), and three controls were subjected to 60-minute sorption tests by placing sorbent samples on oil-seawater mixtures. Kruskal-Wallis H Test and the Mann-Whitney U test revealed significant differences among groups. An equal ratio of SCB and HH had significantly the highest percent sorption, likely due to the lignocellulosic content in SCB and the lipid layer in HH. Cellulose in SCB is suspected to promote water absorptivity and consequently, percent water sorption, while the hydrophobicity of HH possibly caused low percent water sorption. The synthetic sorbent pad exhibited the highest percent oil sorption, which can be attributed to its hydrophobicity, oleophilicity, and large surface area. The incorporation of HH in SCB shows favorable results in diesel oil removal, specifically in an equal ratio. With this, the study can be a basis for the establishment of sorbents incorporating SCB and HH.

Introduction. - The Philippines, being an archipelago, relies heavily on maritime transport for movement, including motorized “pump” boats or *bangkas* powered by diesel-powered outriggers, where spillage usually occurs during refueling and bilge discharge [1]. Vessels caused more than half (55.15%) of the oil spills in the country between 1975 and 2019, and more than three-fourths of which were Tier 1 oil spills (between 1 to 10,000 liters) [2].

Various methods and technologies such as chemical treatment, bioremediation, and physical remediation like skimmers, booms, and sorbents have been applied in the recovery and remediation of oil spills [3,4]. Sorbents are materials used to remove or recover pollutants by absorption, adsorption, or both [5]. Absorption involves the oil penetrating the pore spaces of the material, while adsorption only entails physical accumulation on the surface of the adsorbent [6,7,8].

Effective sorbents should have high hydrophobicity, oleophilicity, uptake capacity, and appropriate efficiency in oil recovery, retention, reusability, and biodegradability [9, 10]. Based on these criteria, synthetic sorbents are the most widely applied materials but they are the not advantageous economically and environmentally, hence there is a rising trend in publications on oil spill cleanup and alternatives [11] Specifically, there is a growing interest in natural sorbents [11,12,13] due to their accessibility, low costs [11,14]; biodegradability, and non-toxicity [3]. However, a disadvantage for most natural materials is low hydrophobicity which reduces potential oil uptake due to competition between seawater and oil molecules [3,11].

Studies [15,16,17] have investigated the sorption ability of various natural materials such as raw sugarcane bagasse (SCB), specifically for oil. It is a fibrous agricultural by-product obtained after sugarcane is crushed for juice extraction [16,18].

SCB and its derivatives have been studied as potential adsorbents in both their raw and modified forms [19]. Ali et al. [15] found that SCB exhibits excellent sorption capacity, exceeding 10 g/g, however, its oil-to-water sorbency ratios were considerably low. SCB can still acquire water in its pores despite having a strong high affinity for oil, which hinders its field application. Ifelebuegu and Momoh [18] reported that the high oleophilicity and hydrophobicity of human hair (HH) resulted in increased oil adsorption and decreased water adsorption once integrated with coconut coir. In order to increase usability of SCB, the current study used SCB with added HH, which are agricultural and human waste, respectively. SCB may be more effective in oil spills with reduced water sorption ability [17] and increased oil sorption capacity by incorporating HH in 1:3, 1:1, and 3:1 ratios [18].

For supplementary data, contact: publiscience@wvc.pshs.edu.ph.

In addition to the multiple studies on SCB [6,16,22] and HH [20,21,23] for oil sorption, this research may offer additional insight into oil spill removal, sorbent materials, and the potential of agricultural waste. The abundance and low-cost of raw lignocellulosic materials and HH are favorable for practical applications and clean-up efforts, specifically in oil-water separation [11,24,25].

The study aimed to determine the sorption percentages of SCB incorporated with HH in varying ratios (1:1, 1:3, 3:1) in diesel oil using 60-minute sorption tests. Specifically, it aimed to:

(i) measure and compute the mean percent sorption (PS) (%), mean percent oil sorption (POS) (%), and mean percent water sorption (PWS) (%) of each treatment and control group;

(ii) compare the mean PS, mean POS, and mean PWS of groups using the Kruskal-Wallis H test; and

(iii) determine which pairs of means are statistically different using the Mann-Whitney U test.

Methods. - The methodology is divided into five (5) parts: preparation, sorption, separation of oil and seawater, computation of parameters, and statistical analysis. The estimated duration of the experiment was four weeks, which included periods for procurement, data gathering, and data analysis.

Preparation. SCB and HH were washed and soaked in distilled water, respectively, and dried under sunlight. SCB was sieved to a particle size of 0.25 mm and randomized using the coning and quartering method. A total of 4 g for each sorbent group (excluding sorbent pads) were wrapped in polypropylene fabric for easy retrieval after sorption. A 3-D sphere was used to shape and pack sorbent bags with consistency and minimal disparity.

The oil-seawater mixtures composed of 200 mL of seawater and 20 mL of diesel oil were prepared in 600 mL beakers and measured with a calibrated toploading balance (Sartorius QUINTIX1102-1S).

Sorption. The sorption test was performed by subjecting the wrapped SCB + HH (1:1) sorbent to the surface of the oil-seawater mixture and allowing it to float freely, following the American Society for Testing and Materials (ASTM) F726-99 - Standard Method for Testing Oil Spill Sorbents [5.] After 60 minutes, the sorbent was removed and drained in a basket for 2 minutes. Finally, the resulting sorbent was weighed using a calibrated analytical balance (KERN ABJ 320-4NM). The same procedures were done for the remaining treatment (1:3 and 3:1) and control groups (SCB only, HH only, and sorbent pads). Six samples were tested for each group. To control the substance sorbed by the polypropylene fabric used to wrap the treatments, six samples of empty polypropylene bags of the same dimensions as those used in wrapping the sorbents were subjected to the same procedures and same experimental conditions. The average weight of the substance sorbed by the empty bag was subtracted from the weights of the sorbent samples.

Separation of Oil and Seawater using Decantation. To obtain POS and PWS values, the remaining oil-seawater mixture was transferred to a separatory funnel, where the mixture was left to rest. The seawater layer was first collected, followed by the oil layer. The separated remaining oil and seawater were individually weighed using a toploading balance.

Computation of Parameters. All variables were measured in grams. PS is the ratio of the substance sorbed by the sorbent to the initial substance in the oil-seawater mixture, disregarding the effect of the polypropylene fabric. It was computed with the formula [20]:

$$PS = \frac{W_a - W_b - W_s}{O_t + W_t} \times 100\%$$

where:
W_a is the weight of the sorbent after sorption,
W_b is the weight of the sorbent before sorption,
W_s is the weight of the substance sorbed by the polypropylene fabric,
O_t is the initial weight of the oil in the oil-seawater mixture, and
W_t is the initial weight of the seawater in the oil-seawater mixture

The POS is a ratio of oil sorbed to the initial oil in the oil-seawater mixture, disregarding the effect of the polypropylene fabric. It was computed with the formula:

$$POS = \frac{O_t - O_r - O_s}{O_t} \times 100\%$$

where:
O_t is the initial weight of the oil in the oil-seawater mixture,
O_r is the weight of the oil remaining in the beaker after sorption, and
O_s is the average weight of oil sorbed by the empty polypropylene bags.

The PWS is the ratio of seawater sorbed to the initial seawater in the oil-seawater mixture, disregarding the effect of the polypropylene fabric. It was computed with the formula:

$$PWS = \frac{W_t - W_r - W_w}{W_t} \times 100\%$$

where:
W_t is the initial weight of the seawater in the oil-seawater mixture
W_r is the weight of the seawater remaining in the beaker after sorption; and
W_w is the average weight of seawater sorbed by the empty polypropylene bags.

For the group sorbent pads, the same formulae were used, but O_s and W_w had no values.

Statistical Analysis. The computed mean values of each group for each parameter were analyzed using the Kruskal-Wallis H test. The Mann-Whitney U test was made to identify which pairs of means were statistically different. All tests were performed using Statistical Package for the Social Sciences (SPSS) (Version 28.0.0.0, IBM SPSS Statistics).

Safety Procedure. Precautionary measures for transport, storage, handling, first aid, personal protective equipment, and disposal were observed and implemented. Diesel oil was placed away from items that can create possible hazards. Safety glasses with side shields, aprons, boots, air-purifying respirators for organic vapors (Elastomeric Half Facepiece Respirators), and gloves were worn throughout the data gathering. Lastly, liquid substances and sorbent waste were handed over to Caltex Station Tabuc Suba and PSHS WVC's Research Assistants, respectively, for proper disposal.

Results and Discussion. - The treatment with an equal ratio of SCB and HH had significantly the highest mean PS and PWS, while the control group sorbent pad had significantly the highest mean POS.

Percent Sorption. The mean PS between the treatment and control groups was significantly different using the Kruskal Wallis H test (H (5) = 26.8393, p = <0.001). The Mann-Whitney U test revealed that the pairs of means that showed statistical differences were T1 and T2, T1 and C2, T1 and C3, T2 and C1, T2 and C2, T3 and C1, T3 and C2, T3 and C3, C1 and C2, and C1 and C3.

Table 1. The Mean Percent Sorption of Treatment and Control Groups.

Group	Mean Percent Sorption (%)
T1 (1 SCB: 1 HH)	16.5783 ± 4.97
T2 (1 SCB : 3 HH)	9.2233 ± 3.78
T3 (3 SCB: 1 HH)	12.9033 ± 1.73
C1 (SCB only)	16.1600 ± 1.08
C2 (HH only)	1.7700 ± 1.90
C3 (Sorbent Pad)	3.9117 ± 0.28

The mean PS of T1 (1 SCB: 1 HH) is significantly higher compared to the PS of T2 (1 SCB : 3 HH), C2 (HH only), and C3 (Sorbent Pad), while it is comparable to the PS of T3 (3 SCB: 1 HH) and C1 (SCB only). This may be attributed to the higher SCB content comprising T1 (1 SCB: 1 HH), T3 (3 SCB: 1 HH), and C1 (SCB only). SCB contains a carbon percentage greater than 50%, providing an initial indication of high lignocellulosic content [18]. SCB is a combination of 40-45% cellulose, 20-30% lignin, and 30-35% hemicellulose [26,27]. Since the groups contain 50% or more SCB, it is supported by its main constituents and polymeric structures, which have a strong influence on the adsorption capacity [28].

The PS of T1 (1 SCB: 1 HH) can also be attributed to the presence of keratin and cuticles covered by a layer of lipid (18-methyleicosanoic acid), which contributes to the hydrophobic and oleophilic characteristics of HH, hence, the ability to sorb large quantities of oil from aqueous solution [29,30,31]. However, despite its porous structure [32], rough texture, large surface area, and the presence of amine (NH–), hydroxyl (OH), sulfide group, S—S, carboxyl group, C—O, and carbonyl (C=O) groups on its surface [21,30,31], which are factors for high sorption affinity of HH, C2 (HH only) shows the lower than expected sorption affinity for HH (Table 1) in contrast to the recommendation of Ifelebuegu and Momoh [18]. Another mechanism may have been involved in T1 leading to improved distribution because SCB particles and/or HH fibers might be optimally more separated in the 50% mixture.

C1 (SCB only) had a significantly higher mean PS compared to T2 (1 SCB : 3 HH). Surface morphology of the sorbent material is a factor that affects oil adsorption [9]. The rough exterior of SCB [15] provides more active sites for oil adsorption which is desirable and linked to high sorption capacity. Moreover, the oil adsorptivity of a natural sorbent is directly dependent on its active surface area [34,35]. Given that the SCB content was reduced when comparing C1 and T2 as well as SCB having better sorption than HH when comparing C1 and C2, it can be implied that reducing the SCB content also diminishes the sorption potential.

C1 (SCB only) had a significantly higher mean PS compared to T3. It can be speculated that this was contributed by SCB's high water absorptivity [18]. It was observed during the experiment that most samples of T3 (3 SCB: 1 HH) and C1 (SCB only) sank to the bottom of the beaker. This phenomenon is in accordance with the study of Ali et al. [15] and supported by Chau et al. [36], where it was stated that when enough water is absorbed, natural cellulose-based absorbents would sink.

Moreover, T3 (3 SCB: 1 HH) was significantly higher than C2 (HH only), an indication that the incorporation of HH to SCB is better compared to HH alone. T3 (3 SCB: 1 HH) is also significantly higher than C3 (Sorbent Pad), suggesting the potential of the sorbent when compared to commercially manufactured sorbent pads. Additionally, C1 (SCB only) is significantly higher than C2 (HH only) and C3 (Sorbent Pad), which means that SCB exhibits better PS compared to the sorbent material HH or sorbent pads. Similar to the previous discussion, these may be attributed to the higher SCB content comprising T3 (3 SCB: 1 HH) and C1 (SCB only) [16].

The treatment and control groups (excluding C3 (Sorbent Pad) which were laid in sheets) were wrapped with a polypropylene fabric using a 3-D printed sphere to maintain consistent bulk density among samples. Bulk density is also a key factor in determining sorbent porosity and sorption capacity. It indicates how much weight of material could be packed per unit volume and is used to determine how much material can fit in the container [37]. Paulauskienė et al. [38] found that sorbents with high sorption capacity exhibit low bulk density values, since in theory, lower bulk density defines higher porosity. To achieve similar packing space and bulk density across samples, a 3D-printed sphere was used to determine the tightness and amount of space the sorbent bags of the treatment and control groups (excluding C3 (Sorbent Pad)) would have.

Percent Oil Sorption. Kruskal-Wallis H test showed a statistically significant difference between the treatment and control groups (H(4) = 15.413, p = 0.004). Using the Mann-Whitney U test, C3 (Sorbent Pad) was statistically different from all treatment and control groups as it had significantly the highest POS (excluding T1 (1 SCB: 1 HH)) from the parameter.

Table 2. The Mean Percent Oil Sorption of Treatment and Control Groups, excluding T1*.

Group	Mean Percent Oil Sorption (%)
T2 (1 SCB : 3 HH)	2.45 ± 1.28
T3 (3 SCB: 1 HH)	1.07 ± 0.78
C1 (SCB only)	1.94 ± 1.03
C2 (HH only)	5.63 ± 5.91
C3 (Sorbent Pad)	59.70 ± 7.47

*T1 was excluded from the POS data analysis due to insufficient number of samples.

It was also found that C3 (Sorbent Pad) had the significantly highest mean POS, which may be due to synthetic sorbents having good hydrophobic and oleophilic properties [24] and high sorption capacity [4]. Sorbent pads are made from engineered polymers with a high surface area, a factor that promotes sorption [39]. Additionally, C2 (HH only) had a large standard deviation (Table 2) which may be due to the small sample size of the study.

Percent Water Sorption. Kruskal-Wallis H test showed a statistically significant difference between the treatment and control groups (H(4) = 14.601, p = 0.004). The Mann-Whitney U test showed that the mean PWS of C2 was significantly lower than those of other treatments — T1 (1 SCB: 1 HH), T2 (1 SCB : 3 HH), T3 (3 SCB: 1 HH), and C1 (SCB only). Furthermore, T1 (1 SCB: 1 HH) had significantly higher PWS compared to T2 (1 SCB : 3 HH) (Table 3).

Table 3. The Mean Percent Water Sorption of Treatment and Control Groups, excluding C3**.

Group	Mean Percent Water Sorption (%)
T1 (1 SCB: 1 HH)	36.65 ± 7.34
T2 (1 SCB : 3 HH)	15.97 ± 13.30
T3 (3 SCB: 1 HH)	30.71 ± 6.65
C1 (SCB only)	29.76 ± 4.35
C2 (HH only)	2.09 ± 1.64

**C3 was excluded from PWS data analysis due to significant outliers.

C2 (HH only), sorbents containing only HH, had significantly lower mean PWS than the other groups. The low sorption of water can be attributed to the hydrophobic property of HH, which is contributed by the layer of lipid that shelters keratin and the cuticle [6] and its affinity for oil [40,41]. In comparison to T1 (1 SCB: 1 HH), T2 (1 SCB : 3 HH), T3 (3 SCB: 1 HH), and C1 (SCB only), the absence of SCB in the C2 (HH only) group entails a lack of potential water absorptivity, whereas SCB is highly capable of 400% to 700% water absorptivity [17].

It was also found that T1 (1 SCB: 1 HH) had a significantly higher mean PWS than T2 (1 SCB : 3 HH). The difference could be explained by the high water sorption capacity of SCB [7, 17] combined with the hydrophobicity of HH [6]. Comparing the two groups, T1 (1 SCB: 1 HH) has one more gram of SCB and one less gram of HH than T2 (1 SCB : 3 HH). It follows that T1 (1 SCB: 1 HH) is able to absorb more seawater. It can be noticed that groups containing 50% or more SCB are comparable and have a mean of 29% PWS or more. This may be due to the SCB's natural sorption capabilities.

Limitations. Considering that this study was conducted at the height of the pandemic, the organic materials were sun-dried instead of oven-dried due to feasibility concerns, specifically, limited access to equipment. Variations in room temperature may have occurred due to ventilation at the data collection site.

Conclusion. - The PS, POS, and PWS of SCB incorporated with HH in varying ratios in diesel oil were investigated to determine its applicability as an oil spill sorbent.

SCB when incorporated with HH resulted in the highest PS and PWS, which can be attributed to the combination of the water absorptivity of SCB and the oleophilicity of HH. In regards to POS, sorbent pads exceeded all other treatment and control groups consisting of organic materials possibly due to its high surface area and synthetic nature.

This study can serve as a basis for the formulation of SCB with HH as viable oil sorbents in diesel oil removal, and when comparing the treatments of the study, an optimal sorbent ratio would be an equal amount of SCB and HH.

Recommendations. - Experiments can be conducted within a day to avoid possible influence in the following days or all control groups can be tested per day for a more accurate comparison with the treatments. The polypropylene fabric in the study may have had an effect on the treatments and results, hence efficient methods to disregard its effect can be implemented, along with more replicates. Excess substance caused by weak capillary forces can be excluded from the sorbed substance of the sample.

The weighing of glassware can be done repeatedly and with minimal movement in the surroundings to reduce the chances of error in the resulting measurement. Further research can be done at a microscopic level to establish the synergistic effect of SCB and HH provided that both absorption and adsorption are present. Additionally, adsorption isotherm modeling and kinetic modeling are suggested to determine maximum sorbent uptake and reaction rate. Future studies can also test variations in oil types and the packing of the materials into the bag. For bulk density, different geometrical shapes can be considered to determine a standard measurement in packing and significant differences with respect to their sorption abilities.

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