Comparison of the percent adsorption of raw corn husk and raw rice husk for bunker fuel

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Abstract

Oil spills are detrimental to the environment and its inhabitants. In this study, raw corn husks (RCH) and raw rice husks (RRH) were used as sorbents for bunker fuel. Adsorption tests were performed by subjecting the sorbents in bunker fuel. The mean percent adsorption of RCH, RRH, and sorbent pad were 10.1%, 3.75%, and 56.8%, respectively. It was found that RCH exhibited a significantly higher mean percent adsorption than RRH which was most likely due to its relatively higher cellulose content. Additionally, sorbent pad exhibited a significantly higher mean percent adsorption than the husks possibly due to its higher saturation point. Although the adsorption percentages of RCH and RRH were significantly less than that of sorbent pads, their ability to adsorb made them viable sorbents for bunker fuel removal, and when compared, RCH would be the better sorbent over RRH.

Introduction. - Oil spill incidents pose a serious threat to the marine environment. These spills may be caused by accidents involving oil tankers and pipes, natural disasters, and runoffs [1]. Spills including crude oil from tankers, refined petroleum products, and heavy fuels such as bunker fuel are a major environmental concern. This is because most components of the oil-like polycyclic aromatic hydrocarbons (PAHs) are toxic to both aquatic and terrestrial organisms, and induce irreversible effects to the environment [2,3]. Bunker C fuel (No. 6 oil), which powers marine vessels, is the most common in these incidents [4]. Bunker fuel evaporates in small percentages and presents a higher viscosity relative to the other oil types [5].

Adsorption is an economically advantageous and eco-friendly approach in remediating oil spill incidents. It is a process wherein oil particles are attracted to the surface of the sorbent. The process relies on the adhesion of the oil particles to the sorbent surface and cohesive properties of oil which allow greater amounts of oil to be retained by the sorbent [8].

Studies have investigated the adsorption capabilities of different agricultural wastes on crude oil [1,7,9]. The use of rice husks and corn husks as sorbents for oil spill remediation removes environmental pollutants while minimizing the negative impacts of burning and disposal of agricultural by-products [10]. It was concluded in the study of Razavi et al. [7] that the oil adsorption capacity of raw rice husk on crude oil was independent of pH. They added that the particle size of the sorbent and viscosity of the oil would significantly affect the adsorption capacity wherein directly proportional relationships would be observed between the adsorptive capability and the two parameters. Biological structures were also found to affect adsorption capacity [11,12]. Furthermore, previous studies have utilized pre-treated husks in removing environmental pollutants such as dyes, heavy metals, and certain organic compounds [1,9]. However, it should be noted that these pre-treatment steps may be time-consuming and costly [10]. Thus, the use of husks in their raw state would be highly advantageous, especially in emergency oil spill situations.

Previous studies have found that cellulose content is higher in raw corn husk (RCH) than in raw rice husk (RRH) [13,14,15,16,17]. It was also observed that when the cellulose content was increased, the adsorption capacity of husks also increased [11,12]. Therefore, it is hypothesized that RCH will exhibit a significantly higher fuel percent adsorption compared to RRH.

This study aimed to determine and compare the percent adsorption of RRH, RCH, and sorbent pads for bunker fuel. It specifically aimed to:

(i) determine the weight of the sorbents before and after adsorption; and

(ii) calculate and compare the percent adsorption of the three sorbents.

Methods. - The corn husks and rice husks were washed, sun-dried, ground, sifted, wrapped in polypropylene fabric, and then submerged in pure

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bunker fuel. Commercially available polypropylene sorbent pads, also wrapped in polypropylene fabric, were used as a positive control. The samples were allowed to drain before weighing to determine the percent adsorption of the three sorbents (RRH, RCH, and sorbent pads). The mean percent adsorption of the three sorbents were then determined and compared using One-Way Analysis of Variance (ANOVA). Ten samples were conducted per sorbent.

Materials. RCH and RRH were gathered from San Joaquin, Iloilo, and Roxas City, Capiz, respectively, while sorbent pads were obtained from the Philippine Coast Guard Station in Bo. Obrero, Iloilo City. Bunker fuel was procured from the Iloilo City Public Safety and Transportation Management Office.

Preparation. RCH and RRH were washed, sun-dried, subjected to grinding, then sifted using a 2 mm sieve. Ground husks then underwent the coning and quartering method thrice for randomization. Five grams of each sorbent was wrapped in polypropylene fabric. Polypropylene fabric was used as a container for easy retrieval of the ground sorbents after submersion in bunker fuel.

Adsorption. Wrapped RCH was soaked in 80.0 g of bunker fuel for 3 hours and was allowed to drip until the point when no further dripping was observed. Finally, the resulting sorbent was weighed using a calibrated digital weighing scale. Similar procedures were followed for the RRH and sorbent pads. Ten samples were tested for each sorbent. To control the effect of the polypropylene fabric on fuel sorption, three samples of empty polypropylene pouches of the same dimensions as those used in wrapping the sorbents were subjected into the fuel under the same experimental conditions. Their weights were then taken, and averaged. The calculated average weight of 10.62 grams was subtracted from the weights of the sorbents wrapped in polypropylene fabric with adsorbed fuel.

Data Analysis. The percent adsorption for each sorbent was calculated using the following formula adapted from the study of Razavi et al. [1]:

$$\% \, Adsorption = \left(\frac{S_t - S_0}{W_{fuel}}\right) \times 100$$

Where:
S_t = the weight (in grams) of the sorbent after adsorption
S_o = the weight (in grams) of the sorbent before adsorption
W_{fuel} = the weight of the fuel before adsorption in grams.

Statistical Analysis. One-way ANOVA was conducted to compare the three mean percent adsorption using Microsoft Excel 2016 with Real Statistics Resource Pack software (Release 7.2) and QI Macros statistical process control (SPC) software package plugin, version 2021.01. The level of significance was at 0.05. The Levene's test was used for the homogeneity of variances and the Tukey test for post-hoc analysis. Both were executed using the same program. To check for normality, the Shapiro-Wilk test was conducted using the software JASP 0.14.1.

Safety Procedure. Excess bunker fuel and used sorbents were stored in a closed container and were handed over to the community waste disposal team.

Results and Discussion. - Table 1 shows the average weights (in grams) of each sorbent before and after fuel adsorption.

Table 1. Mean and standard deviation of the weights before and after fuel adsorption (in grams) of RCH, RRH, and sorbent pad.

Sorbent	Before Adsorption (g)	After Adsorption (g)
RCH	5.00	13.2 ± 1.89
RRH	5.00	8.00 ± 0.78
Sorbent Pad	5.00	50.4 ± 1.74

Figure 1 shows the respective mean percent adsorption of the three sorbents for bunker fuel.

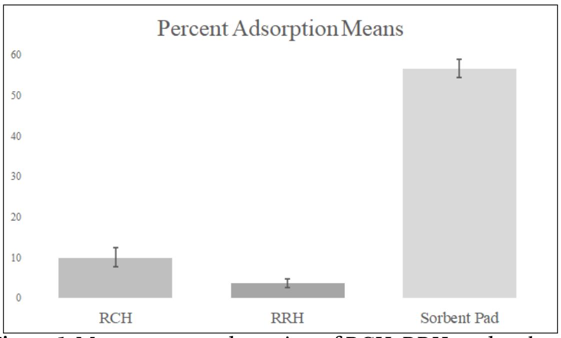

Figure 1. Mean percent adsorption of RCH, RRH, and sorbent pad for bunker fuel.

RCH yielded a mean percent adsorption of 10.1 ± 2.40. The RRH on the other hand had mean adsorption of 3.75% ± 1.03. Finally, for the sorbent pad, the mean adsorption was 56.8% ± 2.29.

Using the Shapiro-Wilk test, data was confirmed to have a normal distribution. Additionally, there was a statistically significant difference between groups as determined by one-way ANOVA ($F(2,27) = 2090.11$, $p = .000$). Data was found to satisfy the assumption of homogeneity of variances through Levene's test ($p = 0.093 > 0.05$). Tukey post hoc test revealed that RCH (10.13% ± 2.40%, $p = .000$) exhibited a significantly higher mean percent adsorption than RRH (3.75% ± 1.03%, $p = .000$), and sorbent pad (56.77% ± 2.29%, $p = .000$) exhibited a significantly higher mean percent adsorption than RCH.

The significantly higher percent adsorption of RCH over RRH could be attributed to the cellulose content of the sorbents. The cellulose content in RCH is generally greater than that in RRH [13, 14, 15, 16, 17], where the mentioned studies only featured either of the husks. In addition to this, characterization studies using the Technical Association of Pulp and Paper Industry (TAPPI) method of identifying the chemical composition of husks revealed that cellulose in corn husks reached 31-39% while only a maximum of 31%

was present in rice husks [18, 19]. Cellulose was found to play a key role in maintaining the mesopore structure of activated carbon as a sorbent [11]. Mesopores function in accelerating diffusion into micropores and increasing the equilibrium coverage of the micropore surface which contains adsorptive sites wherein the inner layers possess higher adsorption energies [12].

According to the International Tanker Owners Pollution Federation Limited (ITOPF) [8], sorbent materials for oil spills should attract oil to their surface or incorporate the oil in the material itself. RCH and RRH exhibited mean percent adsorption of 10.19% ± 2.40 and 3.76% ± 1.02, respectively. The exhibited percent adsorption, although low, can qualify RCH and RRH as sorbent materials. In addition, there is no basis for comparison for the RRH results since the methods used in this study were not similar to other related studies. With this, due to the husks' biodegradability, high supply, simple preparation, low cost, but low adsorption capacity, RCH and RRH could be potential sorbents only for emergency bunker fuel spill situations, in cases when the commercially used sorbent pads are unavailable.

It was also found that the sorbent pad exhibited a significantly higher percent adsorption compared to the other two organic sorbents. This was concurrent with the information that polypropylene sorbent pads can recover up to 20% more oil than natural organic sorbents [17]. Although natural-based materials are inexpensive, abundant, and environmentally friendly, their relatively lower oleophilic property makes their adsorption capacity inferior to some synthetic materials which are engineered for the sole purpose of adsorbing fuels [18, 19]. Furthermore, the difference in the packing of the sorbent pad and the husks may have affected the surface area of each sorbent, which is another factor that influences adsorption [8]. Since the sorbent pads were laid in sheets, they may have had greater surface area than the ground husks, therefore yielding a significantly greater percent adsorption

In conducting the experiments, the sorbent pad was first tested to identify the ideal contact time and bunker fuel dosage, which is the least possible amount of fuel and time for the sorbent pad to be completely soaked. The contact time should ensure the sorbent has reached its maximum saturation [23]. It was found out that five grams of sorbent pad were completely saturated when immersed in 80 grams of bunker fuel at the 3-hour mark. A contact time of three hours, bunker fuel dosage of 80 grams, and initial sorbent weight of five grams were uniformly followed for the final data gathering for all three sorbents.

The dripping time after adsorption used for the final data gathering was 15 minutes which was observed during the preliminary data gathering to be the point of no dripping. Dripping time should reach the point of no dripping to ensure that the fuel loosely held by the sorbent is lost to report an accurate adsorption capacity [23]. This can also be backed by the study of Said et al. [24] which also utilized the same length of fuel dripping.

To avoid the interference of the possible fuel adsorption of the polypropylene fabric that was used to wrap the sorbents, its mean fuel adsorption was also separately measured thrice following the same contact and dripping times as the final data gathering. The mean fuel adsorption of the polypropylene fabric was then subtracted from the total weight of the sorbent after the fuel adsorption in calculating for the percent adsorption of the final data.

Limitations. Due to the lack of resources, mathematical models were not used in presenting the results. In addition, there was no basis for comparison for the RRH results since the methods used in this study were not similar to other related studies. Lastly, due to the unavailability of the necessary equipment, the uniformity of the packing of the sorbents in the polypropylene fabric was not followed wherein the husks were in powder form while the sorbent pads were laid in sheets when subjected to bunker fuel.

Conclusion. - The adsorption percentages of RCH and RRH were significantly less than that of sorbent pads, and when compared, RCH would be the better sorbent over RRH. Despite the limited inclusion of adsorption parameters, this study showed a simple preliminary measure of screening oil adsorption capacities of ground sorbents for possible usage in oil spills.

Recommendations. - It is recommended that future studies conduct adsorption isotherm modelling to investigate the interaction mechanism between the adsorbent and the adsorbate. Furthermore, future studies can also test different physical modifications such as size and surface area variations to RCH and RRH and determine any significant differences with respect to their adsorption capacities. In addition, it is recommended that the size and morphology of the tested sorbents be characterized by electron microscopy techniques and their chemical composition by spectroscopic techniques like infrared spectroscopy. It is also recommended that when comparing different sorbents, the packing should be uniform for all tested sorbents. Lastly, it is recommended to test the adsorption capacities of RCH and RRH on other oil pollutants in an oil/water mixture.

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