Comparison of diesel oil removal properties of primary and secondary leaf fibers of *Ananas bracteatus*

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Abstract

The increasing dependence of humans on oil-based energy constitutes the risk of oil spills which pose hazards to the environment. Some existing oil spill cleanup methods apply chemicals that are harmful to marine life. Pineapple leaf fibers (PALFs) have been used as a sorbent and they showed excellent oil sorption, but are yet to be separated into primary and secondary leaf fibers. *Bastos* are coarse while *liniwan* are fine fibers which affect their oil sorption capacity since they have varying fiber diameters and surface area. In this study, primary (*bastos)* and secondary (*liniwan*) PALFs were used as sorbents and subjected to diesel oil. The mean sorption capacity by *bastos*, *liniwan*, and sorbent pad were 13.76 g/g, 14.09 g/g, and 4.43 g/g, respectively. *Bastos* and *liniwan* were found to have no significant difference between their mean oil sorption capacity and exhibited a significantly higher mean oil sorption capacity than the sorbent pads. This implies that both the *bastos* and *liniwan* can be used as sorbents for potential diesel oil spills. It is suggested to use *bastos* more as an alternative in diesel oil removal since it is not used in other industries as compared to *liniwan*.

Introduction. - The Philippines is an archipelagic country, and shipping is the primary mode of inter-island transportation. Marine transport is also the backbone of international trade and the global economy [1]. It is also located at the Coral Triangle, which is an area of importance as it is recognized as the global center of marine biodiversity [2]. The increasing dependence of humans on oil-based energy has raised concerns about the risk of increasing oil spills.

The International Tanker Owners Pollution Federation recorded a total of 15,000 tonnes of spilled oil in 2022 which was caused by tanker incidents globally [3]. The Philippine Coast Guard, as secured by the National Operation Center for Oil Pollution (NOCOP), has recorded 553 oil spills as of 2019, more than half of which are caused by vessel oil spills (55.15%). Vessels usually transport petroleum products including diesel oil, which is also the top-imported petroleum product in the country in 2022 [2,4]. Moreover, MT Princess Empress was carrying 800,000 liters of industrial fuel oil when it sank in February 2023. This resulted in threats to fishing communities and biodiversity in 20 marine protected areas [5].

Oil spills can have catastrophic consequences for both the environment and human health. Oil spills are major water pollutants that kill marine organisms; with some that are suitable for human consumption [6]. These pollutants may spread and reach rivers and other aquatic habitats, posing a hazard to our environment [7]. Ecological changes, primarily the loss of key organisms from a community, may also be observed as a result of oil spills [8].

Dispersion and in-situ burning are some of the current solutions to oil spills. However, dispersion uses chemicals that are harmful to marine life and in-situ burning produces gasses that are harmful to our atmosphere and toxic to human bodies, so it is important to find methods to mitigate the effect of oil pollution and also recover the spilled oil simultaneously such as the process of sorption through organic sorbents [9,10]. Organic sorbents have been emerging as possible alternatives for oil spill cleanup due to their availability, eco-friendliness, and low cost [11].

Oil sorption is an alternative method used to recover oils with the help of sorbent materials that act like a sponge [12]. Synthetic sorbents such as polypropylene are commonly used in oil sorption because they have a high sorption potential, but they are non-biodegradable and expensive [13]. This led researchers to study biodegradable and low-cost sorbents such as lignocellulosic materials.

Plant waste fibers, which are characterized as lignocellulosic materials, are resources composed primarily of cellulose, hemicellulose, and lignin. These can be derived from plant substances such as agricultural residues [14]. The Philippines is the world's second-largest producer of pineapple plant residue, wherein the fibers derived from the pineapple leaves are usually dumped for composting, thus making them agricultural wastes which would make them useful for biowaste utilization [15]. Previous studies have utilized pineapple leaf fibers (PALFs) as biosorbents for oil such as the study of Gomes et al. [16] who found that the peat (commercial sorbent) and the curaua PALF showed similar sorption capacity. Moreover, Ekwonu et al. [17] utilized PALFs blended with polyethylene/polypropylene sheath core composites (ES) as sorbents for diesel and automotive gas oil. Cheu et al. [18] also used pineapple leaves but are chemically pretreated to exhibit higher oil sorption capacity.

According to the study of Sena Neto et al. [19], leaves of *Ananas bracteatus*, more commonly known as Red Spanish Pineapple, have been found to have higher cellulose content than other genotypes of pineapple. As higher cellulose content contributes to higher sorption potential [20], *Ananas bracteatus* leaf fibers can provide more alternative sorbent materials to other genotypes of PALFs that had already been utilized as oil sorbents [16,17,18].

PALFs are classified according to their fineness: the coarse fiber with a higher fineness value (primary PALF or *bastos*) and the fine fiber with a lower fineness value (secondary PALF or *liniwan*) [21]. Fineness is related to the fiber thickness or diameter [22]. As fineness decreases, the diameter of individual fiber decreases and therefore increases the surface area available for sorption. *Liniwan* having a lower fineness makes it a more ideal material in the textile industry compared to *bastos*.

Studies on oil removal using PALF have not separated the *bastos* and *liniwan* [16,17,18]. Due to their difference in fiber fineness, which affects their surface area [22], the individual sorption performance of *bastos* and *liniwan* must be investigated to provide an alternative sorbent material for oil sorption instead of using all fiber parts of the pineapple leaf.

This study aimed to determine and compare the percent diesel oil removal of *bastos*, *liniwan*, and sorbent pads. Specifically, this research sought to:

(i) determine the mean fiber diameter (μm) of *bastos* and *liniwan* through ImageJ analysis based on scanning electron microscopy (SEM);

(ii) determine the mean difference between the mean fiber diameters (μm) of *bastos* and *liniwan* using independent samples t-test;

(iii) determine the mean oil sorption capacity (g/g) and mean percent oil removal of the control (sorbent pads) and treatment groups (*bastos* and *liniwan*);

(iv) determine the mean difference of the oil sorption capacity (g/g) and percent oil removal (%) of the control and treatment groups using one-way ANOVA.

Methods. - The fibers were sent for SEM imaging and the fiber diameter of *bastos* and *liniwan* was measured using an image processing software (ImageJ). Ten replicates of sorbent from the treatment and control groups were allowed to sorb oil at a constant contact time. The mass of sorbent before and after sorption was measured to get the sorption capacity and percent oil removal.

Materials. Bastos and *liniwan* were procured from a pineapple fiber-weaving business in Balete, Aklan as thread-like fibers which are readily available for utilization while sorbent pads were obtained from Philippine Environmental & Technical Systems and Services, Inc. Diesel oil was procured from SEAOIL - Tagbac in Jaro, Iloilo.

Preparation. Bastos, *liniwan*, and sorbent pads were cut into 1 to 2 cm [23], and 0.5 grams of each sample was placed in a 50-cm^3 metal mesh bag [9,10,24,25]. Diesel oil with a volume of 200 mL was poured into each 250 mL beaker (Pyrex, Germany) [26]. Three samples of empty metal mesh baskets were immersed in the oil under the same experimental conditions. The mass of oil removed was then taken and averaged and was then subtracted from the mass of the sorbents after sorption. The average mass of oil removed by the mesh basket was subtracted from the mass of oil removed by the sorbents encapsulated in the metal basket with sorbed oil.

Fiber diameter. Dry fiber samples of *bastos* and *liniwan* were sent to the University of the Philippines Visayas Regional Research Center laboratory in Miagao, Iloilo for scanning electron microscopy (SEM, Hitachi SU3500) imaging. The mean diameter of each fiber type was calculated by measuring it three times at different sections of the SEM image using ImageJ software (Version 1.54f).

Preliminary Test. Three samples for each sorbent type were prepared to determine the dripping time of the samples and the amount of oil removed by the metal mesh baskets. Beakers with 200 mL of oil were prepared for each sample. Sorbents were hung on a metal stand for 60 minutes [16]. Then, sorbents were hung above the beakers and the dripping time was recorded until no further dripping [27]. The sorbents were then weighed and recorded.

Sorption test. The *bastos* sorbent was soaked in 200 mL of diesel oil for 60 minutes and was allowed to drip until the point when no further dripping was observed (50 minutes). Finally, the resulting sorbent was weighed using a calibrated analytical balance (KERN ABJ 320-4NM). Similar procedures were followed for the *liniwan* and sorbent pads. Ten samples were tested for each sorbent.

Data Analysis. The oil sorption capacity and percent oil removal [24] for each sorbent were calculated using the following formula:

$$\text{Sorption capacity (g/g)} = \frac{S_T - S_O}{S_O}$$

$$\text{Percent removal (\%)} = \frac{S_T - S_O}{O_I} \times 100$$

Where:
S_T=the mass (in grams) of the sorbent after sorption
S_o=the mass (in grams) of the sorbent before sorption
O_I=the mass (in grams) of the sorbate before sorption

Statistical Analysis. ImageJ and Microsoft Excel 2016 were used to calculate the mean fiber diameter, mean sorption capacity, and mean oil percent removal of the sorbents, respectively. An Independent t-test was conducted to compare the mean difference between the mean fiber diameters in Jamovi 2.3.18. One-way ANOVA and Games-Howell post hoc test were conducted to compare the three mean sorption capacities and oil percent removal using Jamovi 2.3.18.

Safety Procedure. Excess diesel oil and used sorbents were stored in a closed container and handed over to the Chemistry Science Research Assistant for proper disposal.

Results and Discussion. - The surface morphology of both fibers was found to be closely similar to each other in reference to their microfibrillar structure, exhibiting rectangular, rough surfaces as can be seen in Figures 1 and 2. *Bastos* and *liniwan* revealed defined block-like structures which contribute to a rougher surface [25]. According to Ekwonu et al. [17], this unique block-shaped structure contributed to the excellent oil retention property of the PALF. This block-like structure is the leaf epidermal tissue fragments which are characterized by a reticular aspect pattern [28].

Based on the results of the ImageJ analysis, the mean fiber diameters of *bastos* and *liniwan* were 109.25 ± 11.49 μm and 115.41 ± 14.00 μm, respectively. No statistically significant difference was found between the fiber diameters of both fibers based on their t-test results (p = 0.587). *Bastos* and *liniwan* were found to have similar fiber fineness as described by their similar mean fiber diameters. Fiber fineness is a factor in the sorption mechanism as finer fibers constitute more surface area for higher oil uptake [22]. According to Carvalho et al. [21], the secondary PALF or *liniwan* is used in textile production because of its low fiber fineness while the primary PALF or *bastos* are not being used in textile production; however, the ImageJ results contradict this as *bastos* and *liniwan* showed similar fiber diameters. In their optical microscopic images, *bastos* and *liniwan* were found to have similar fiber diameters, which have some correlation to fiber fineness [22]. Finer fibers contribute to smaller fiber diameters, allowing them to have higher surface area and more available sorption sites for sorption [29].

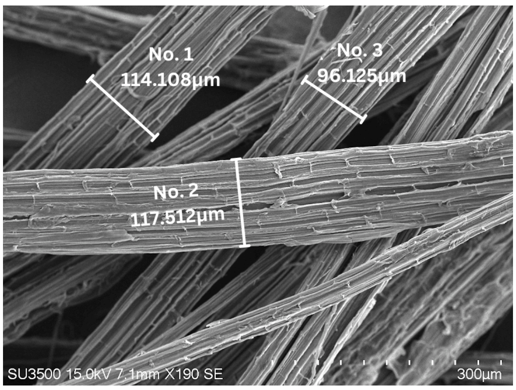

Figure 1. SEM image of primary PALF (*bastos*) at 190x magnification.

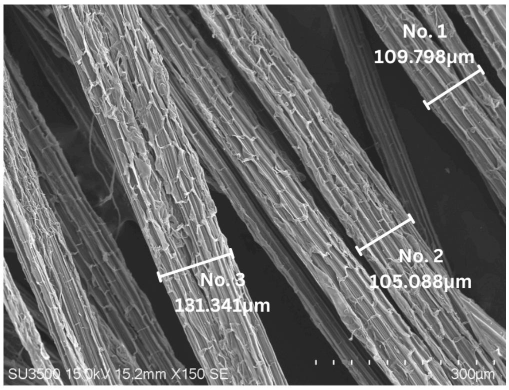

Figure 2. SEM image of secondary PALF (*liniwan*) at 150x magnification.

The sorption capacity and percent removal values of *bastos* and *liniwan* have been found to be significantly higher than that of the sorbent pads, while it was also found that there is no significant difference between *bastos* and *liniwan*. *Bastos* yielded a mean sorption capacity of 13.76 ± 1.53 g/g. The *liniwan* sorbent on the other hand had a mean sorption capacity of 14.09 ± 0.84 g/g. Furthermore, the sorbent pad yielded a mean oil sorption capacity of 4.43 ± 0.34 g/g.

Bastos yielded a mean percent oil removal of 4.15 ± 0.46%. *Liniwan,* on the other hand, had a mean percent oil removal of 4.25 ± 0.25%. Finally, for the sorbent pad, the mean percent oil removal was 1.34 ± 0.10%. Figure 3 shows the respective mean percent oil removal (%) of the three samples for diesel oil.

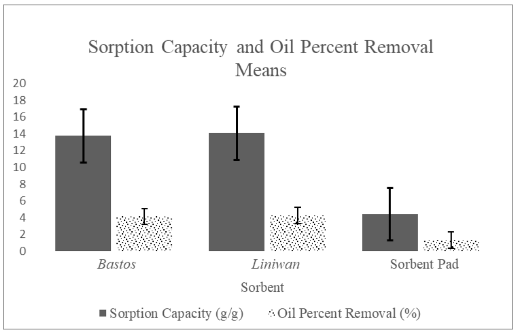

Figure 3. Mean sorption capacity (g/g) and mean percent oil removal (%) of *bastos, liniwan,* and sorbent pads for diesel oil.

There was a statistically significant difference between groups as determined by One-way ANOVA (F(2,27) = 668.5725, p = 0.0001). Games-Howell post hoc test revealed that *bastos* and *liniwan* have no significant difference in their sorption capacity and percent oil removal (p = 0.8277). *Bastos* exhibited a significantly higher sorption capacity and mean percent oil removal than the sorbent pad (p < 0.001). In addition, *liniwan* (p < 0.001) exhibited a significantly higher sorption capacity and mean percent removal than the sorbent pad (p < 0.001). *Ananas bracteatus* PALFs have significantly higher mean sorption capacity and percent oil sorption than commercial sorbent pads, thus they can be used as a sorbent for potential diesel oil spills. Additionally, the results imply that both the *bastos* and *liniwan* have similar levels of effectiveness in terms of oil sorption.

Both *bastos* and *liniwan* are capable of sorption for diesel oil. The mechanism of oil sorption by *bastos* and *liniwan* can either be by absorption, adsorption, capillary action, or a combination of the aforementioned. The fiber diameter has some correlation with the fiber cross-sectional areas which affects the sorption mechanism of PALFs. Finer fibers contribute to a smaller diameter [22], which leads to more available sorption sites leading to a higher sorption capacity [29]. The sorption process in natural fibers can be a product of physical factors, transport of oil molecules to the surfaces of the sorbent, and chemical factors, which involve the Van der Waals interaction between the oil and the sorbents [18,30]. As *bastos* and *liniwan* are both natural fibers collected from *Ananas bracteatus* leaves, the mechanism involved in the sorption process can be explained by the said factors. Sample granulometry is a significant factor in the percent oil removal of PALFs for diesel oil as it affects the surface area of the samples [16].

This study was able to determine the sorption capacity and percent oil removal of *bastos* and *liniwan* collected from *Ananas bracteatus* comparing it to sorbent pads. The sorption capacity and percent oil removal of *liniwan* do not have a significant difference from that of *bastos*. In addition, there is a significant difference between the sorption capacity and percent oil removal of the treatment (PALFs) and the control group (sorbent pads). The fiber diameters from the SEM imaging correlate with the sorption capacity and percent oil removal of the fibers since the sorption capacity and percent oil removal of *bastos* and *liniwan* have no statistical mean difference and their mean fiber diameters also have no statistical mean difference. The results showed that both *bastos* and *liniwan* may be used as alternative materials for the removal of diesel oil. Although, *bastos* and *liniwan* were found to have no significant mean difference, thus, *bastos* may be used as an alternative sorbent to oil spills rather than *liniwan* since the latter is used as raw materials for textile production.

Limitations. Even though the fiber diameter of raw *bastos* and *liniwan* was determined, only partial areas of the fiber samples were assessed for SEM analysis. Moreover, this study only utilized 1-2 cm lengths of cut PALFs, the optimal granulometric sizes for the maximum sorption capacity of PALFs were not determined with the absence of sorption tests of varying granulometric sizes.

Conclusion. - As *bastos* and *liniwan* have the same performance in the removal of oil, *bastos* may be utilized as an alternative sorbent material for oil spills as *liniwan* already have their use in the textile industry.

Recommendations. - Future studies may utilize more areas of the PALFs to be subjected to SEM imaging to minimize error in randomization and to have a more accurate presentation of the surface morphology of PALFs. Moreover, sorption tests may include quantifying for fiber fineness and varying sample granulometry to determine which granulometric category constitutes the optimal sorption capacity of PALFs. In addition, other statistical tools which include more decimal places for calculations such as SPSS and RStudio may be used for the data analysis since Jamovi 2.3.18 can only cater up to three decimal places. Furthermore, future studies can also test the sorption capacity of the samples in an oil-water mixture and test more oil types such as bunker fuel, jet fuel, and others.

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