ABSTRACT

Experiments on the potential of Cogon grass (Imperata cylindrica), a weed harmful to other plants, for use as a low-cost and biodegradable oil sorbent were carried out under various spill conditions. Flowers of Cogon grass adsorbed much larger amount of high-viscosity lubricating oil (57.9 g-oil/g-sorbent) than that adsorbed by Peat Sorb (7.7 g-oil/g-sorbent), a commercial oil-sorbent based on peat. However, the flowers adsorbed only 27.9 g of low-viscosity crude oil/g-sorbent. In an oil-water system, the amount of oil adsorbed was influenced by the level with which the two were mixed: vigorous stirring reduced the sorption capacity by 36%. The high sorptive capacity of the flowers can be attributed to their hydrophobic nature and good oil-wettability. The flowers showed good buoyancy even after 24 hours of shaking under conditions that simulated water ripple (gentle wavy motion) in sea, which suggests their potential in combating oil spills both on land and in water.

Keywords: Sorbent; Oil spill; Oil sorption; Cogon grass; Imperata cylindrica

INTRODUCTION

Oil spills are one of the major sources of environmental pollution in land and marine environments. Improving the techniques for controlling and removing oil spills is an active area of research. One of the approaches to control is to develop oil sorbents that can remove oil from a spill site completely. Based on the nature of raw materials, oil sorbents can be grouped into three major classes, namely inorganic minerals, synthetic organics, and natural organics. A comprehensive review of this subject can be found in Adebajo et al.\(^\text{1}\). Commercial oil sorbents
Commonly used by many petroleum companies are synthetic sorbents made of polypropylene and polyurethane. They have good hydrophobic and oleophilic properties, but their non-biodegradability is a major disadvantage, particularly because they need to be disposed of properly after use. This limitation has led the search for alternative methods using biodegradable material such as lignocellulosic fibers of agricultural residues or weeds. In many cases, the material is locally and cheaply available, the main costs being mainly those of collections and preparation. It is much easier to compost lignocellulosic fibers than synthetic polymers after use, which reduces the hazard and cost associated with incineration or other means of disposal. Moreover, cellulosic products exist in fibrous form and can be easily made into mats, pads, or nonwoven sheets. A number of natural sorbents have been studied for use in cleaning up oil spills. Some of them have good oil sorption capacity, but they also adsorb water at the same time, which is a disadvantage when they are used in aqueous environment.

Several studies to find sorbent materials from natural organics with high oil sorption capacity, high hydrophobicity, and good buoyancy are described below. Basically they can be grouped into (1) explorations of new plant material and (2) chemical treatment of known plant material. Choi and Cloud found that milkweed floss (Asclepias) fiber adsorbed significantly larger amount of crude oil (approximately 40 g oil/g fiber) than such artificial fibers as nylon, polyester, acetate, viscose rayon, or polypropylene (typically below 25 g/g). Nonliving biomass of Salvinia sp. was identified to adsorb only 4.8 g crude oil/g biomass, and Suni et al. reported that cotton grass (Eriophorum vaginatum) removed up to 20 times its own weight of diesel oil. Recently, Annunciado et al. found silk floss (Chorisia speciosa) fibers to have a very high oil sorption capacity (approximately 85 g/g). Meanwhile, other research groups have been trying to make some plant material more hydrophobic by chemical treatment: wood bark saturated with transition metal ions, acetylation of cotton fiber, rice straw, and sugarcane bagasse. Although these chemical treatments significantly improved sorption capacity, the result was a more expensive sorbent product. Other important factors that need to be considered are local availability and abundance of the sorbent materials in the area of spills, particularly in remote areas where options to transport bulky material to the site are limited. Therefore, identifying such material for use as a clean-up tool for oil spills is of significant commercial interest.

Cogon grass (Imperata cylindrica) was ranked as one of the ten worst weeds of the world particularly because it can spread, colonize, and subsequently displace other desirable vegetation. Cogon grass regenerates very rapidly from its underground rhizomes and responds with flowering to such control measures or forms of stress as burning, overgrazing, drought, and repeated slashing. It grows in various ecosystems from the dry to the moist natural areas, and has been reported as a weed in 73 countries, mostly in Africa, Australia, southern Asia, and the Pacific. This paper discusses the potential use of Cogongrass as oil sorbent in cleaning up oil spills on land and in water.

MATERIAL AND METHODS

Sorbent material

The grass was obtained from a plot of marginal land in Serpong (Banten, Indonesia). A commercial natural oil sorbent (Peat Sorb), a processed peat, provided by a sales agent in Jakarta, was used for comparison. The grass was air-dried, its flowers (spikelets) were separated from the stem, and the stem was cut into pieces 2-4 mm long. Peat Sorb was ground in a mill (Quacker City Mill model 4-G, Philadelphia, USA) and sieved in a laboratory test sieve (Retsch, Germany) to obtain particles of 500-600 μm. All such material was stored in a dessicator; it was removed from the desiccator and air-dried overnight at room temperature before use. Moisture content of the grass flowers after such pretreatment was typically 6%-8%.

To quantify buoyancy, 25 mg of grass flowers was placed in a 1000 mL glass beaker containing 500 mL water or a mixture of 450 mL water and 50 mL oil and the contents stirred for 60 min at 72 rpm. At the end of the test, the part that remained afloat was removed, dried, and weighed to calculate the buoyancy percentage.

Specific gravity of the grass flowers was measured using a picnometer with hexane (SG =
specific gravity was measured using a picnometer (Duran, 25 mL and 10 mL). In order to know the tendency of oil to evaporate, oil samples were placed in a glass dish 9 cm in diameter and 1.5 cm deep, and the loss in weight after 24 hours of storage at room temperature and pressure was recorded.

Sorbents are generally not effective in cleaning up highly viscous or heavy oils. These oils do not adhere to the sorbent readily owing to their poor wettability; on contact with water, highly viscous oils tend to sink partly and heavy oils tend to sink completely. The oil should not be highly volatile either lest it should evaporate quickly. The physical characteristics of the oils used in the experiment are shown in Table 1.

To measure the area of a cross section of a broken fiber of the grass flower, a scanning electron microscope (Philips 515) was used. The specimen was prepared by immersing the material into liquid nitrogen and grinding it to powder in a mortar. Gold-coated samples were then mounted on a universal base and placed in a vacuum chamber at a high pressure ($1.33 \times 10^5$ Pa or $10^{-4}$ Torr).

Test oils

The following oils were used for the sorption tests: light crude oil (Cemara crude oil), automotive diesel oil (Solar), lubricating oil (Mesran Super 20W-50) obtained from Pertamina (a major Indonesian petroleum company), and heavy crude oil (Petani crude oil) obtained from PT CPI (Chevron Pacific Indonesia). Kinematic viscosity was determined at 40 °C by a viscometer (Koehler Instruments, model K-23429, Germany) and specific gravity was measured using a picnometer (Duran, 25 mL and 10 mL). In order to know the tendency of oil to evaporate, oil samples were placed in a glass dish 9 cm in diameter and 1.5 cm deep, and the loss in weight after 24 hours of storage at room temperature and pressure was recorded.

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Table 1. Oil types and their properties

<table>
<thead>
<tr>
<th>Oil types</th>
<th>Specific gravity</th>
<th>Kinematic viscosity (cSt)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petani crude oil</td>
<td>0.865</td>
<td>35.43</td>
<td>2</td>
</tr>
<tr>
<td>Cemara crude oil</td>
<td>0.824</td>
<td>1.90</td>
<td>20</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>0.840</td>
<td>4.15</td>
<td>2</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>0.884</td>
<td>175.60</td>
<td>0</td>
</tr>
</tbody>
</table>

*Viscosity at 40 °C
\*After 24 hours at room temperature

All the oils had a specific gravity lower than unity, and therefore they would not sink in water. At 30 °C, their viscosity was low enough so for them to adhere to the sorbents easily, with the exception of Petani crude oil, which had to be warmed to 35 °C for it to be fluid enough to be adsorbed. Data on oil volatility show that during 20 minutes of the sorption experiment, the weight loss due to evaporation of oil was less than 0.3% of the original weight. The above properties indicate that these oils are suitable to be removed using sorbent as a clean-up tool.

Sorption experiments

To assess the capacity of the biomass to adsorb oil in absence of water (dry system), a procedure specifically set for loose particulate sorbents was used\textsuperscript{39}. The sorbent (0.25 g for grass and 1 g for Peat Sorb) was placed inside a wire basket (pore size 150 μm), made of steel wire, 6.2 cm in height and 4.5 cm in diameter. The basket was...
then dipped in a 1-liter beaker containing 500 ml of oil. Because it is bulky, smaller amount of grass flower was used in this experiment. The beaker was in turn placed in an agitator (floculation tester, SBS Instruments) and the liquid stirred at 100 rpm for 20 minutes, considered long enough for the sorbent to be saturated with oil. The basket containing the sorbent was then raised, the oil allowed to drain by gravitation for 1 minute, and the basket weighed. An empty basket, subjected to the same process to account for oil deposited onto metal surfaces, functioned as a blank. The amount of oil adsorbed was measured as the weight gained after sorption, expressed in grams per gram of dry sorbent. All sorption tests were run at 30°C ± 0.5°C, except those for Petani crude oil, which were run at 35°C ± 0.5°C because the oil is highly viscous. These temperatures were chosen to represent ambient temperature in the tropics.

In oil–water systems, only two types of oils (lubricating oil and Cemara crude oil) were further tested to represent high- and low-viscosity oils respectively. The experiments were carried out at three levels of mixing (static, gentle, and vigorous) in a 1000 mL glass beaker containing 450 mL tap water and 50 mL oil. For static condition and gentle mixing, the grass flowers were poured onto the surface of the oil and, after saturation, collected in the metal basket described above. For static condition, the contents were not mixed at all; for gentle mixing, intended to simulate waves in the marine environment, the beaker was shaken in an orbital shaker (Cole Parmer 51300-05) at 72 rpm. Vigorous mixing, to simulate the environment in which the oil is completely dispersed in water, was carried out in a Dynamic Heidolph MR 2002 mixer and a stirring bar operating at 1000 rpm; the sorbent remained in the basket, the same as in dry oil system. The apparatus was observed every 20 minutes over an hour to see the effect of contact time on the amount of oil adsorbed. The sorbent saturated with oil was then raised to allow the excess oil to drain by gravitation for 4 minutes, and weighed. Longer time was provided for draining in the oil–water system than the dry system to make sure that the sorbent was free of any drops of liquid adhering to it. Water was extracted from saturated sorbent with fluids as described in ASTM[20], using a Dean-Stark glass still, with a mixture of xylene and toluene (80:20, v/v) as a solvent. The results of all measurements were presented as average of three replicates. The bars denote standard deviation of the replicates.

RESULTS AND DISCUSSION

Characteristics of the Cogon grass flower

The grass was identified at Herbarium Bogoriense, Indonesian Institute of Sciences, as *Imperata cylindrica* (L.) Beauv, known as Alang-alang or Ilalang (Indonesian) or Cogon grass (English).

Figure 1. Cogon grass and its hairy flower: (a) Cogon grass growing on marginal land, (b) grass flower at ×40 magnification, (c) cross-section of the rod-like grass flower fiber at ×1000 magnification showing the fiber's hollow structure.

Figure 1 shows the morphology of the grass and a magnified image of flower parts. Figure 1a shows Cogon grass growing on a piece of marginal land. The plant is a slender, flat, linear-lanceolate stemless grass, less than a meter tall, arising from a thick underground mat of rhizomes. A complete morphological description of this grass can be found in Aguilar[21]. Figure 1b shows the characteristics of a single hairy flower (spikelet) about 8–10 mm long. Its snowy white color suggested a waxy coating. The importance of the
waxy surface to the hydrophobic and oleophilic properties of cotton and milkweed was reported by Choi and Cloud\(^6\); it is believed to confer similar properties on Cogon grass. Figure 1c shows the hollow structure (lumen) of the hairy parts of the Cogon grass flower. The same kind of rod-like fiber found in kapok, milkweed, and cotton has been demonstrated to contribute to the high oil-sorption capacity owing to increased surface area and enhanced capillary action\(^6\).

The grass flower was very bulky and its density was estimated to be 0.66 g/cm\(^3\), approximately the same as that of hexane in which the grass flower dispersed evenly in the liquid phase. After saturation with oil, the volume of the grass flower is usually smaller. Therefore, in its application as oil sorbent, this material can be compacted to some extent, but not so much that little space is left for the oil. After saturated with oil, the sorbent needs to remain buoyant in water for some time to facilitate its collection. Observations indicated that in the beaker containing only water, the grass flower remained above the surface of the water but in the presence of oil, it would concentrate in the oil phase above the water phase. The grass flowers remained in these positions even after 24 hours of gentle shaking that simulated waves, suggesting that the buoyancy was 100\% for both the grass flower in water and the grass flower saturated with oil in the oil–water mixture. Buoyancy over such a long period is an important feature of the Cogon grass flower, making it easier to collect the grass and remove it from water bodies. The value of BET surface area for nitrogen sorption of the grass flower was estimated to be 1.84 m\(^2\)/g. This value was obtained for the grass flower in a powder form, as BET surface area for large particle cannot be determined directly.

Wettability of the grass flower in oil or in water is an important parameter when the sorbent is to be used in aquatic environment. A good oil-sorbent should adsorb a great deal of oil but only a small amount of water. Wettability can be measured in terms of the level of fluid penetration in a column filled with powder or fiber. According to Perry and Green\(^18\), the capillary action in such a system is controlled by the viscosity of the fluid, capillary radius, surface tension between the liquid and air, contact angle between the liquid and solid surfaces, and time. In addition, Choi and Moreau\(^9\) demonstrated that capillary action took place not only in the internal lumen of a hollow fiber but also within the voids (capillary bridges) between fibers. In our experiment, both mechanisms can be expected to operate because of the presence of the hollow structure of the grass flower fiber shown in Figure 1c. Hexane, as a non-polar organic solvent, was used to represent various oils tested, while water represented the polar fluid.

A large difference in the level of penetration of the fluids in the column between hexane (\(h^2 = 400 \text{ cm}^2\)) and water (\(h^2 = 90 \text{ cm}^2\)) showed that the grass flower is wetted far more easily by hexane than by water (Figure 2), indicating that the grass flower has good wettability in oil and is hydrophobic and supporting the results shown in Figure 3, namely that the grass flower adsorbed as much as 57.9 g oil/g but only a small quantity of water (1.5 g/g). This oil sorption capacity is much higher than that of milkweed floss (40 g/g) reported by Choi and Cloud\(^6\).

**Effect of sorbent materials**

Results of the experiment with the dry oil system, i.e. sorption characteristics of different sorbents in an oil bath without the presence of water, are given in Figure 3. The experiment was
meant to simulate the cleaning up of an oil spill on dry land. The flower parts of the grass adsorbed more lubricating oil (57.9 g/g) than that adsorbed by the stem (5.9 g/g) or by Peat Sorb (7.7 g/g), a commercial natural oil sorbent based on peat. Other oils (diesel and crude oils) were adsorbed in smaller amounts. In another part of this paper, it will be shown that sorption preferences of some oils for different sorbents are somehow related to viscosity. The greater adsorptive capacity of the grass flower than the stem or Peat Sorb suggested that the surface area of the flowers was much larger than that of the other two. Also, the grass flower was more hydrophobic, retaining the least amount of water (1.5 g/g), compared to the stem (9.2 g/g) or Peat Sorb (5.9 g/g). Hydrophobicity is an important quality required of an effective sorbent for its application in aquatic environment. Ribeiro et al.\(^6\) and Annunciado et al.\(^8\) used the same commercial product, Peat Sorb, for comparison. They found a rather wide range of oil sorption capacity, from 2.7 to 9.8 g/g, and our result falls within this range. These differences occurred possibly due to variations in particle sizes of the pretreated Peat Sorb and the types of oil tested.

**Effect of mixing in oil–water systems**

Experimental results in the dry oil system and in the oil-in-water system for high-viscosity oil (lubricating oil) and low-viscosity oil (Cemara crude oil) are summarized in Figures 4 and 5 respectively.

![Figure 4](image4.png)

**Figure 4.** Sorption of high viscosity lubricating oil by Cogon grass flower under various spill conditions. Dry = oil only, stirred at 100 rpm; Static = oil in water, no mixing; Gentle Mixing = oil in water, shaken at 72 rpm; Vigorous Mixing = oil in water, stirred at 1000 rpm. 20, 40, 60 mins denote sorption period.

![Figure 5](image5.png)

**Figure 5.** Sorption of low viscosity crude oil by Cogon grass flower under various spill conditions. Dry = oil only, stirred at 100 rpm; Static = oil in water, no mixing; Gentle Mixing = oil in water, shaken at 72 rpm; Vigorous Mixing = oil in water, stirred at 1000 rpm. 20, 40, 60 mins denote sorption period.

The highest amount of lubricating oil was adsorbed in the dry oil system; in the presence of water, the amount of oil adsorbed decreased slightly with static condition and gentle stirring, but significantly (up to 36%) with vigorous stirring. Similar trends were observed for Cemara crude oil. The dry-oil system adsorbed more oil because in this case, most of the surface area of the grass flower was available for the oil whereas in the oil–water system, there was competition between water and oil for the same surface areas, and parts of them would be occupied by water. These differences, however, were not significant, because the grass flower, being highly hydrophobic, adsorbed very small amount of water (Figure 3).

The different mixing regimes in the oil–water system affected the amount of oil adsorbed. The static system was a two-phase system where no mixing was involved; gentle mixing involved shaking at 72 rpm; and vigorous mixing involved stirring at 1000 rpm. As indicated above, only vigorous stirring significantly reduced the amount of oil adsorbed (by 36%). This can be explained as follows. The mixing enhanced mass transfer of air into the liquid phase and increased dispersion of air bubbles. However, more vigorous stirring lead to more air bubbles, resulting in increased resistance on part of the oil to attach to the surface of the sorbent. In the static system or gently stirred system, there were no air bubbles, and oil was directly in contact with the sorbent all the time.

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In the vigorous stirred system, a film of oil would form at the gas–water interface of the air bubbles, constituting a discrete phase. Consequently, contact between oil and the sorbent would occur only when turbulence (the result of vigorous stirring) brought the sorbent and air bubbles in close proximity. In addition, the diameter of the air bubbles was likely to be much larger than the pore openings of the sorbent, preventing the air bubbles from penetrating and reaching the internal surfaces of the pores. The above factors influenced not only the amount of adsorbed oil but also the kinetics of oil uptake at 20, 40, and 60 minutes. Figures 4 and 5 show, beyond 20 minutes, the amount of adsorbed oil increased only slightly. Studies by Annunciado et al. also confirm that further observation up to 24 hours did not result in any significant increase in oil uptake because the sorbent had almost reached its saturation equilibrium by 20 minutes.

**Effect of oil viscosity**

Whereas adsorption of oil onto sorbent surfaces is dominated by hydrophobic interaction and van der Waals force, absorption takes place within the porous matrices by diffusion. Besides, as previously mentioned, capillary movements would also take place whenever the sorbent material is in the form of fibers. All of the above sorption mechanisms (wettability, diffusion in porous matrices, and capillary action) are known to be affected by oil viscosity. In this study, within the range of viscosity tested, the amount of oil adsorbed by the grass flower suggests a direct relation to oil viscosity at the temperature of contact. Cemara crude oil, the least viscous (1.9 cSt), was adsorbed the least (27.9 g/g) whereas lubricating oil, the most viscous (175.6 cSt), was adsorbed the most (57.9 g/g).

**CONCLUSIONS**

It is concluded that the characteristics of the sorbent material, nature of oils, and spill conditions influence the effectiveness of oil sorbent. Cogon grass (*Imperata cylindrica*) proved to be an excellent oil-sorbent under different spill conditions. In addition to low cost, the grass is more environment-friendly because it is relatively biodegradable whereas synthetic polymers, the commonly used alternative, are not. Grass flowers showed high sorption capacity for various crude oils and oil products because the flowers were highly hydrophobic and easily wetted by oil. The grass material also showed good buoyancy even after 24 hours of shaking that simulated sea waves, suggesting the material's potential in combating oil spills not only on land but also in water.

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