EXPERIMENTAL EVALUATION OF A NATURAL HOLLOW HYDROPHOBIC-OLEOPHILIC FIBER FOR ITS POTENTIAL APPLICATION IN NAPL SPILL CLEANUP[1]

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ABSTRACT

Non-aqueous phase liquid (NAPL) spills on water and land are of major environmental concern. One of the most economical and efficient means for the removal of the spilled NAPL is to use hydrophobic-oleophilic sorbents. Natural, agricultural products have potential to be a substitute for commercial synthetic absorbents in NAPL pickup and recovery. One of these natural agro-products that have excellent oil sorption capacities is Kapok (Ceiba pentandra), a cellulosic silky-cotton fiber.

This paper presents the sorption capacities of Kapok, the reusability of Kapok and its hydrophobicity-oleophilicity for various NAPLs. Both loose and packed Kapok assemblies were examined. The NAPLs investigated were tetrachloroethylene (PCE), diesel and HD-30 engine oil (HD-30).

The NAPL sorption capacities of packed Kapok assemblies were found to be 75, 55 and 45 g/g for PCE, HD-30 and diesel, respectively. Two-thirds of the sorption capacities of virgin packed Kapok assemblies could be retained even at the 8th reuse cycle. Oil sorption capacities of the loose Kapok assembly reached 115 and 45 g/g for HD-30 and diesel, respectively, on dynamic water surface. No thin oil film on water surface was observed after NAPL sorption, when initial oil added in water was less than 30 g/500 mL and 1 g loose Kapok assembly was used.

1. INTRODUCTION

NAPL (non-aqueous phase liquid) spills are one of the knotty environmental pollution problems of the world. Huge amount of oils and oil products are spilled into the sea and thousands of NAPL spills occur inland each year. The adverse impacts to the ecosystem and human health call for effective cleanup technologies to remove NAPLs from contaminated sites. One of such technologies involves the use of absorbent materials.

Absorbent materials are promising in oil spill remediation because of their abilities in removing NAPLs from the spill sites. The favorable properties of a good NAPL absorbent material include excellent NAPL sorption capacity, absorbent reusability, hydrophobicity-oleophilicity as well as biodegradability (Teas *et al.*, 2001; Reynolds *et al.*, 2001).

Some natural agricultural products are potential absorbents for NAPL spill cleanup, with an advantage over the synthetic absorbents of their intrinsic biodegradabilities. Among them, rice straw, corn cob, cotton, milkweed floss, kenaf, and wool fibers have been employed as sorbents in oil spill cleanup (Choi and Cloud, 1992; Choi, 1996). For example, milkweed and cotton were found to absorb significantly more oil compared to commercial synthetic sorbent materials (Choi and Cloud, 1992; Sun *et al.*, 2002; Choi, 1996; Kobayashi *et al.*, 1977). Kapok is also an agricultural product, which is cultivated in Southeast Asia, Sri Lanka, other parts of East Asia, and Africa. In Southeast Asia, it is abundant in supply and inexpensive. However, its potential use as an absorbent for NAPL spill cleanup has not been systemically investigated compared to other agro-based oil absorbents.

This paper presents the results of a recent study which investigated the maximum sorption capacity, reusability and hydrophobicity-oleophilicity of Kapok. Three different NAPLs were examined in this study, namely tetrachloroethylene (PCE), diesel and HD-30 engine oil (HD-30). The effects of packing density of Kapok assembly, surface properties of Kapok fibers, and properties of NAPLs were discussed.

2. MATERIALS

2.1. Kapok fibers

Kapok are silky fibers that clothe the seeds of the ceiba tree of the family Bombacaseae. Kapok fibers have rich oiliness and do not have high strength and, therefore cannot be spun economically. It is conventionally used as a stuffing, especially for life preservers, bedding, and upholstery, and for insulation against sound and heat. The Kapok fiber has a hollow structure (as shown in Figure 1) with external radius around 8.25 (±4) _m, internal diameter around 7.25 (±4) _m, and length around 25 (±5) mm. Combined with the specific material density of 1.3 g/cm^3, large pore volume in Kapok assembly is available for NAPL sorption. Typical analyses indicate that the Kapok fibers comprise 64% cellulose, 13% lignin and 23% pentosan. Besides these constituents, they also contain wax cutin on the fiber surface which makes them water repellent notwithstanding they are preponderantly composed of cellulose (Kobayahi *et al.*, 1977). The Kapok fibers used in this study are products of Thailand. Before they were used in this study, all dust and lumps had been removed.

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[1] Disclaimer: This manuscript is designed to present the perceptions and conceptions of the authors on the subject matter covered. It is intended to illustrate the potential application of an agro-based fiber in the cleanup of oil spills. The views and opinions presented are those of authors and do not represent the views, opinions, or policies of the International Oil Spill Conference or its sponsors.

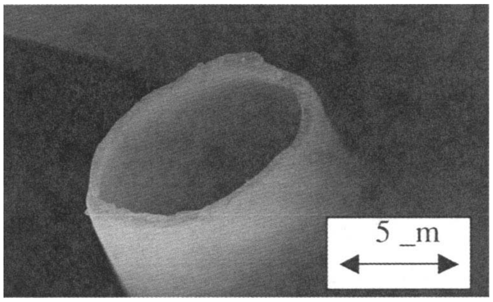

FIG. 1. THE SEM IMAGE OF SINGLE KAPOK FIBER.

2.2. NAPLs

Three kinds of NAPL, namely PCE, diesel and HD-30, were employed to investigate the sorption capacities of Kapok in this study. Among them, PCE was selected for its higher density than water. It represents the category of dense non-aqueous phase liquids (DNAPLs) that are often used as industrial solvents. Diesel and HD-30 belong to the category of light non-aqueous phase liquids (LNAPLs). Diesel represents low-viscosity oils such as light crude oil, kerosene and gasoline. HD-30 is a good surrogate for viscous oils such as heavy crude oil, intermediate fuel oil and bunker c fuel oil. The densities of the three NAPLs were measured. Their viscosities were measured using viscolab viscometer (VL-4100) from Cambridge Applied Systems, Inc. Their surface tensions were measured using a dynamic contact angle meter and tensiometer (DCAT 11) from DataPhysics instruments Gmbh. The measured physical characteristics of these three NAPLs as compared to water were listed in Table 1.

Table 1. Characteristics of liquids used

Liquids	Density (g/cm³) (±1%)	Viscosity (10^{-3}Ns/m²)(21-C) (±1.5%)	Surfacetension (mN/m)(21-C) (±1%)
PCE	1.62	0.52	26
Diesel	0.92	2.00	27
HD-30	0.94	110.00	23
Water	1.00	1.00	73

3. METHODOLOGIES

3.1. Determination of maximum sorption capacity

The procedure for determination of maximum sorption capacity followed the standard method F726 described in ASTM (1998). Different quantities of Kapok were packed in 200-cm^3 test cells to produce different packing densities ranging from 0.015 to 0.05 g/cm^3. The lowest packing density (i.e., 0.015 g/cm^3) represented the Kapok assembly in its natural state. The Kapok-filled test cells were lowered into the liquid bath so that they were just submerged into the liquid with their top surface exposed to the overhead air. This avoided air entrapment in the Kapok assemblies during oil sorption. After soaking in the liquid bath for 15 min for PCE and diesel, and 24 hours for HD-30 (more time was needed for the saturation of packed Kapok by HD-30 because of its higher viscosity), respectively, the test cells were lifted above the NAPL bath, allowing the free draining liquids to drip out from the test cells for 1 min. The 1-min dripping time was once adopted by Choi (1996). The test cells were weighed and the amount of NAPL retained in each test cell was calculated. The NAPL retained in the test cells were then squeezed out through centrifugation at 3000 rpm (220 g) for 30 min for recovery. In addition to sorption capacity by mass, volumetric sorption capacity was also determined, which expresses the sorption capacity in terms of volumetric ratio of the liquid absorbed to the total volume of Kapok assembly (the volume of a test cell).

3.2. Evaluation of Kapok reusability

This study determines the extent to which an absorbent can be reused. One of the criteria used in judging the suitability of an absorbent for reuse is the number of cycles it can endure without becoming unusable due to tearing, crushing, or other general deterioration. Other factors are the rate of decrease in its NAPL sorption capacity and the percentage of NAPLs that can be removed with reasonable effort and equipment (ASTM-F726, 1998). In this test, the Kapok material mechanically pressed for NAPL recovery was reused in the same oil sorption experiment as that detailed in Section 3.1, for up to 8 cycles.

3.3. Selectivity test

Selectivity is the ability of a sorptive material to preferentially absorb one material over another. For instance, some oleophilic agro-based materials will, to varying degrees, selectively absorb oil over water. This makes these materials attractive sorbents in oil spill cleanup. The selectivity test was aimed at investigating the selectivity of Kapok for absorbing oil spilled on water and its oil sorption capacity under this condition.

Diesel and HD-30 were examined in this experiment. Different volumes of diesel or HD-30 were poured onto 500-mL tap water in 2-L glass beakers (cross-sectional area is 123 cm^2), which were then placed on an orbital shaker shaken at 100 rpm/min. After attaining steady condition, 1-g loose Kapok was evenly spread on the liquid surface. After 15 min, all fibers were picked out and put into a pre-weighed wire basket and allowed for free draining. At the end of 1-min free draining, the Kapok-filled wire basket was transferred to a pre-weighed stainless container and the total mass of them was recorded. To separate the liquid from the wetted Kapok, the Kapok-filled wire basket was then centrifuged for 30 min at 3000 rpm. At the end of centrifugation, the liquid recovered from Kapok was measured and analyzed for water and diesel or HD-30 contents. The quantity of water in the recovered liquid was measured using an ASTM 100-mm cone-shaped centrifuge tube according to the standard method D 4007 described in ASTM (1998). This water represented the amount of water pickup by Kapok during the sorption test. The mass of diesel or HD-30 recovered was computed as the difference between the total mass of liquid absorbed by Kapok and the mass of water pickup.

4. DISCUSSIONS

4.1. Maximum sorption capacity

The maximum sorption capacities of packed Kapok assemblies with different packing densities were compared in Figure 2 for diesel, HD-30 and PCE, respectively. It was found the sorption capacities by mass decreased with the increment of the packing density in all NAPL samples. The PCE sorption by mass was significantly greater than those of diesel and HD-30 over entire range of packing densities investigated. The greater density of PCE was believed to be responsible for it. When the packing density was less than 0.025 g/cm^3, Kapok assemblies demonstrated better sorption capacity for HD-30 than that for diesel. It was believed to be due to the higher viscosity of HD-30, which constrained the draining of HD-30 in the 1-min dripping time.

In terms of volumetric sorption capacity, the PCE and diesel sorptions also depended on packing density, although not as significant as that measured based on sorption by mass. The volumetric sorption capacities of Kapok assemblies for PCE were lower than those for diesel at packing densities less than 0.04 g/cm^3. This was believed to be due to the higher density of PCE, which could cause considerable compression on Kapok assemblies and consequently reduce the available pore volume for PCE sorption. The contraction of fiber assembly after liquid absorption was also demonstrated by most other natural fibers, which was observed by Jacob (2002). For HD-30, however, no relationship between packing density of Kapok assembly and the volumetric sorption capacity was observed. This phenomenon could be due to the relatively high viscosity of HD-30. From the viewpoint of maximum sorption capacity of packed Kapok assemblies, the optimal Kapok packing densities for diesel, PCE and HD-30 sorptions are between 0.025 and 0.040 g/cm^3, 0.035 and 0.040 g/cm^3 and 0.015 and 0.040 g/cm^3, respectively.

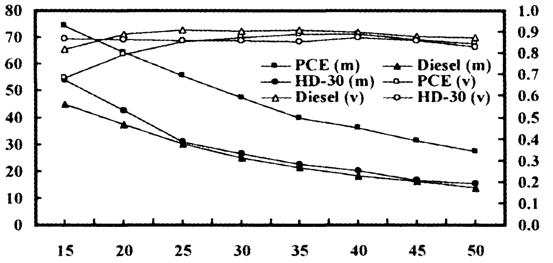

FIG. 2. MAXIMUM NAPL SORPTION CAPACITIES OF PACKED KAPOK ASSEMBLIES FOR THREE NAPLS.

4.2. Reusability of Kapok

Figures 3 and 4 show the NAPL sorption by packed Kapok assemblies for a total of eight cycles for diesel and PCE, respectively. At the 8th cycle, the Kapok assemblies could retain at least two thirds of its initial sorption capacities. Therefore, the good reusability of Kapok indicated that the material could be applied as efficient oil absorbent for several uses (Radeti_, *et al.*, 2003).

The rates of decrease in the sorption capacity of packed Kapok assemblies were observed to be dependent on packing density. The Kapok assemblies with low initial packing densities showed the greater decrease in NAPL sorption capacities. For example, the sorption capacities of the reused fiber assemblies in samples with initial packing densities of 0.015 to 0.030 g/cm^3 were observed to decrease significantly. The capillary force, weight of the liquid and centrifugal force were believed to be responsible for the decrease in sorption capacities by decreasing the effective pore volume of the Kapok assemblies. The sorption capacity of less viscous liquid was governed by the balance between capillary force and the gravity of liquid in the pore space of Kapok assemblies according to capillary principle proposed by Washburn (1921). During the sorption equalization, the numerous liquid bridges were formed between neighboring fibers because of interfacial interaction between liquid surface and fiber surface, which tended to pull fibers together. Simultaneously, the elastic and viscoelastic deformation of the fiber resisted the decrease of inter-fiber distance. Consequently a critical inter-fiber distance could be reached at equilibrium. As a result, the fiber assemblies became more compact and reduced the total effective pore volume of the fiber assemblies for subsequent uses. Centrifugal force contributed more for the sorption decrease compared with other two factors. The centrifugal force resulted in a large increment in compressive pressure on the fiber assemblies of up to 220 times in 1 min. With the forced draining of the absorbed liquid out from the pore space of fiber assemblies, the distance between adjacent fibers decreased significantly. Simultaneously, the deformation of individual fibers under excessively high pressure also contributed to the decrease in effective volume for subsequent liquid sorption. This deformation was not fully reversible due to the hysteresis of the stress-strain relationship for the fiber deformation (Skelton, 1975). Additionally, residual oil trapped in the lumen of Kapok fibers also occupied some pore spaces which could not be fully drained out from the dead end of lumen formed by the folded fibers, as evidenced by the SEM image presented in Figure 5. This further limited subsequent sorption capacity of Kapok assemblies. In summary, the decrease in the effective volume was believed to be responsible for the decrease in the sorption capacity from the second sorption cycle, particularly for loose Kapok assemblies.

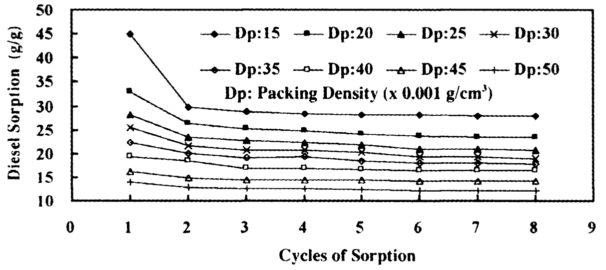

FIG. 3. REUSABILITIES OF PACKED KAPOK ASSEMBLIES FOR DIESEL.

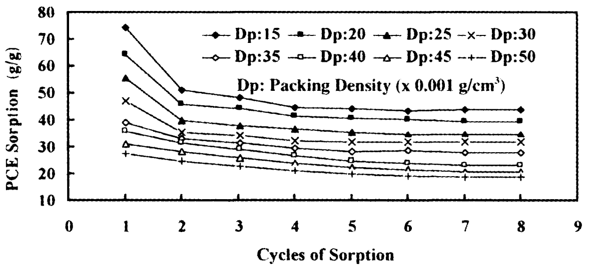

FIG. 4. REUSABILITIES OF PACKED KAPOK ASSEMBLIES FOR PCE.

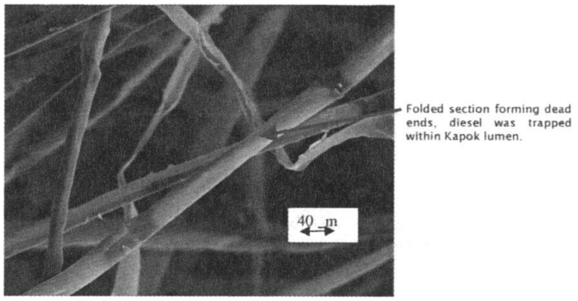

FIG. 5. SEM IMAGE OF USED KAPOK

4.3. Hydrophobicity-oleophilicity of Kapok

The oil sorption characteristics of Kapok in the water bath containing different amounts of oil are illustrated in Figures 6 and 7 for diesel and HD-30, respectively. Similar to the observation reported by Johnson (1973), both diesel and HD-30 absorbed on Kapok increased with the increasing amount of oil available in water until their sorptions reached maximum values. The quantities of water pickup were consistently less than 3 g/g in the experiments. The water picked up was believed to adhere on the external surface of the test apparatus rather than be absorbed by Kapok fibers, because the quantity did not vary with the increment of oil spilled in water. At low quantity of oil in water, almost all oil added was absorbed by Kapok fibers as shown in the insets of Figures 6 and 7. For example, in the case of diesel, there was no visible oil film observed after the wetted Kapok was lifted from the liquid bath. This indicated that the thickness of oil film left on the water bath was less than 0.05 _m, as concluded by Fingas (2000) who observed appearance of oil film on a calm water surface. The selective sorption of oil from water was believed due to the hydrophobic-oleophilic surface properties of the Kapok fiber. It is also worth to note that the maximum HD-30 sorption was significantly greater than that observed in the test condition described in Section 3.1. This phenomenon was not exhibited by diesel sorption in this study. The higher viscosity of HD-30 was postulated to be responsible for the considerably larger sorption capacity. To completely understand and quantitatively analysis the phenomena observed in this experiment, more theoretical and experimental investigations are needed.

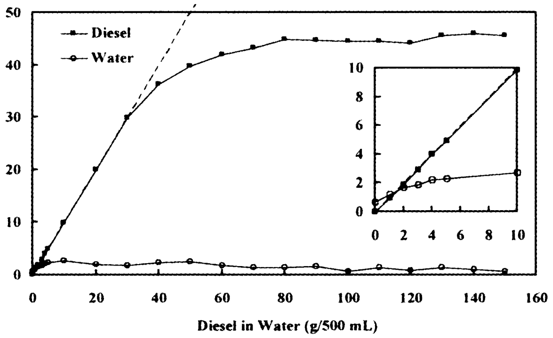

FIG. 6. DIESEL SORPTION (THE DASH LINE IN THE INSET PICTURE IS DIAGONAL OF THE SQUARE).

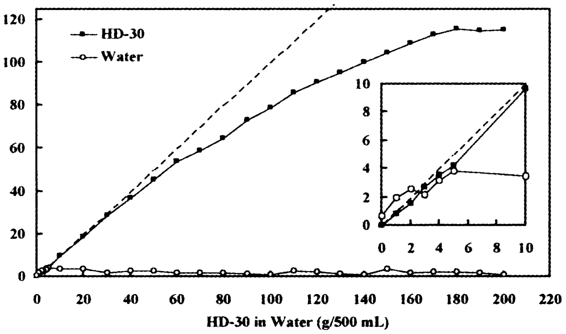

FIG. 7. HD-30 SORPTION (THE DASH LINE IN THE INSET PICTURE IS DIAGONAL OF THE SQUARE).

CONCLUSIONS

This paper presents the oil sorption capacities of packed and loose Kapok assemblies. Three NAPLs, namely diesel, HD-30 and PCE, were investigated to determine the potential use of Kapok in oil spill cleanup. Kapok showed excellent sorption capacity for the three NAPLs. The optimal Kapok packing densities for diesel, PCE and HD-30 sorptions are between 0.025 and 0.040 g/cm^3, 0.035 and 0.040 g/cm^3 and 0.015 and 0.040 g/cm^3, respectively. Packed Kapok assemblies also demonstrated good reusability. They retained at least two thirds of the initial NAPL sorption capacity of Kapok at the 8th reuse cycle. In selectivity experiments, the sorption capacities of loose Kapok fibers reached about 45 and 115 g/g for diesel and HD-30, respectively. But the water pickup in selectivity experiments was consistently less than 3 g/g. The hydrophobic-oleophilic characteristics of Kapok fiber surface were believed to be responsible for the excellent selectivity manifested in the experiments. This study showed that Kapok was a promising material as commercial absorbent for the cleanup of spilled NAPLs. More theoretical and experimental works should be further carried out to investigate the sorption mechanism under different scenarios.

BIOGRAPHY

Xiaofeng Huang was bom on August 18, 1973 in Jilin of China. He received his Bachelor of Engineering in harbors, water channels and coastal engineering from Wuhan University, China, in 1997. He received his Master of Engineering in geological engineering from China University of Geosciences, China, in 2002. Since December 2002, he has been pursuing his PhD degree in the field of environmental engineering under the supervision of Dr. Teik-Thye Lim at Nanyang Technological University, Singapore.

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