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Natural Sorbents in Oil Spill Cleanup

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■ Milkweed (*Asclepias*) fiber and cotton fiber sorbed significantly higher amounts of crude oil than polypropylene fiber and polypropylene web from the surface of an artificial sea water bath containing crude oil and from a crude oil bath. Milkweed sorbed approximately 40 g of crude oil/g of fiber at room temperature. The oil sorption capacity of kenaf core material was comparable with that of polypropylene web with high-viscosity Bunker C oil. Only a slight variation was observed in the oil sorption of the natural fiber sorbent by Soxhlet extraction and water-soaking treatments before the sorption process. However, alkali-scouring treatment significantly reduced the oil sorption capacity of milkweed and cotton fiber. It was shown that with the aid of suitable mechanical retrieval equipment, sorbed crude oil can be recovered from milkweed and cotton so the sorbents can be recycled several times for oil spill cleanup. The results suggested that a total or partial substitution of commercial synthetic oil sorbents by natural sorbent materials could be beneficial in the oil spill cleanup operation by improving the efficiency of oil sorption and by incorporating other advantages such as biodegradability.

Introduction

In March 1989 the *Exxon Valdez* incident spilled 11.2 million gallons of crude oil into the coastal waters of Prince William Sound, AK, causing severe environmental damage (*1*). The demolition of oil storage tanks in Kuwait during the war in 1991 spilled several hundred million gallons of oil into the sea. In addition, oil spills onto land are also common occurrences even though most spills are usually small (*2*).

The presence of sorbent materials in an oil spill area facilitates a change of phase from liquid to semisolid (*3*). Once this change is achieved, the removal of the oil by removal of the sorbent structure is not difficult. While hydrophobicity and oleophilicity are primary determinants of successful sorbents, other important factors include retention of oil over time, recovery of oil from sorbents, amount of oil sorbed per unit weight of sorbent, and reusability and biodegradability of sorbent (*2–5*).

Oil-sorbent materials can be categorized into three major classes: inorganic mineral products, organic synthetic products, and organic vegetable products (*4, 5*). Mineral products include perlite, vermiculites, sorbent clay, and diatomite (*2, 5*). These materials do not show adequate buoyancy retention and their oil sorption capacity was generally low (*5*). Among synthetic products, polypropylene and polyurethane foam are the most widely used sorbents in oil spill cleanup because of their highly oleophilic and hydrophobic properties (*4, 6*). A disadvantage of these materials is that they degrade very slowly as compared with mineral or vegetable products. It has been reported that organic vegetable products such as straw, corn cob, and wood fiber showed poor buoyancy characteristics, relatively low oil sorption capacity, and low hydrophobicity (*5*).

On the other hand, Johnson et al. (*7*) later showed the potential for the utilization of cotton fiber in oil spill cleanup. More detailed information is needed, however, before any further application of cotton fiber can be made in oil spill cleanup. Kobayashi et al. (*8*) examined a hollow cellulosic kapok fiber. According to their results, the oil sorption of kapok fiber used in a mat, block, band, or screen was approximately 1.5–2.0 times greater than that of polypropylene mat, which sorbs 11.1 g of B-heavy oil and 7.8 g of machine oil in water.

Milkweed floss (*Asclepias*), which is cultivated or naturally grown in some states in the United States, is also a hollow cellulosic material (*9*). Kenaf is another cellulosic material readily available in some states. These natural sorbents have hydrophobic properties before any treatments due to their surface waxes. Milkweed floss, especially, is expected to have high oil sorption capacity because of its high wax content and its hollow structure similar to kapok. Nevertheless, no work has been reported on the oil sorption capacity of these materials. If these natural sorbents show high oil sorption capacity, then they can be used to substitute non-biodegradable synthetic materials in oil spill cleanup.

Therefore, the purpose of this research was to study the oil absorbency of milkweed floss, cotton, and kenaf in a simulated seawater bath containing crude oil and in a pure oil bath to examine the feasibility of using these sorbents in oil spill cleanup.

Experimental Section

Sorbent Materials. Descriptive characteristics of the sorbents used in this study are given in Table I. The use of polypropylene materials allowed comparison of natural fiber sorbents with commonly used sorbent structures. Natural fibers used in the study had undergone little processing, thus preserving the natural waxes on the fiber surfaces, which enhance oleophilicity and hydrophobicity. To elucidate the effects of these substances, oil sorption of cotton fibers and milkweed floss was also tested after solvent extraction and after scouring. Soxhlet extraction was carried out by the method described in ASTM D2257-80 (*10*) using 1,1,2-trichloroethane. Scouring was done using a solution containing 2% NaOH and 0.5% Na_2CO_3 at pH 13 at boiling temperature.

Since sorbents may encounter water before oil in a spill cleanup, it is important to know the oil sorption characteristics of water-soaked sorbents. Cotton fiber, milkweed floss, polypropylene web, and milkweed/polypropylene web were tested for oil sorption both in the dry state and after being soaked for 10 min in the artificial seawater.

Crude Oil Samples. The specifications of three crude oil samples, which were obtained from Placid Refining Co., Port Allen, LA, are listed in Table II. In the early stages of an oil spill, lighter weight hydrocarbons are evaporated before any possible cleanup operation can take place (*11*). In order to simulate this situation and to minimize experimental variations, crude oil samples were placed in an

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Table I. Specifications of Sorbent Materials

fiber types	shape	specification	abbreviation	fineness (denier)	length, cm
cotton	fiber	cellulosic fiber	COT	2.3	2.23
milkweed	fiber	cellulosic fiber	MW		3.0
kenaf	fiber bundle	cellulosic fiber	KF		5–10
kenaf	woody core	cellulosic material	KC		0.5–1.0
polypropylene	fiber	polypropylene	PP3	3.0	0.5
	fiber	polypropylene	PP15	15.0	47.6
	nonwoven web	polypropylene	PPW		
milkweed and polypropylene	nonwoven web	milkweed (60) polypropylene (40)	MP		

Table II. Specifications of Crude Oil Samples

	API gravity (60 °F)	viscos KIN_{cst} (100 °F)	spec grav (60 °F)	wt loss, %	
				after 24 h	after 48 h
No. 2 fuel oil (diesel)	35.7	3.93	0.846	6.00	6.40
light crude oil	34.2	6.46	0.854	7.50	10.50
No. 6 fuel oil (Bunker C)	6.3	1024 (122 °F)	1.027	0.04	0.04

efficient hood for 48 h, as described elsewhere (*7*). The weight loss of oil samples during the ventilation was considerable for the two low-viscosity crude oils (diesel and light crude) but not for the high-viscosity oil (Bunker C), as shown in Table II. The majority of the weight loss occurred within 24 h.

Procedure. A 500-mL sample of artificial seawater was placed in a 1-L glass beaker, as described in AATCC 106-1981 (*12*). The desired amount of oil (10, 20, 30, 40, or 50 g) was added to the beaker. The beaker containing crude oil and artificial seawater was mounted in a shaking apparatus (Eberbach Corp.). Approximately 1 g of a sorbent material was placed in the system, which was shaken for 10 min at 102 cycles/min. The wetted sorbent material was weighed after being drained for 1 min in the sustainer. Water content of the sorbent was analyzed by the distillation technique described in ASTM D95-70 (*13*). A mixture of toluene and xylene (20/80, v/v) was used as the carrier solvent. The amount of oil sorbed by the sorbent was determined by subtracting the water content and the initial sorbent weight from the total weight of the wetted sorbent. The quantity of oil was recorded as grams per gram of sorbent. For some of the milkweed floss samples, the bath was prechilled to 5 ± 2 °C in the refrigerator and small amounts of ice were added in the bath during the shaking to keep the temperature constant. At least two replications were carried out for each sample.

In order to study oil sorption capacity of sorbents without the water medium, a simple procedure was used. A 100-mL sample of diesel or light crude oil was placed in a 200-mL beaker before any sorbent was immersed in the bath. After shaking and draining as described above, the amounts of oil sorbed by the sorbent were determined by a gravimetric method.

Recovery of Sorbed Oil and Reusability of Sorbents. Another set of specimens was tested to determine recovery of oil sorbed in the sorbent and reusability of sorbents. With 40 g of light crude oil in the artificial seawater bath, the same sorption procedure was used, but water content was determined by evaporation in the hood, as described in the previous study (*7*), rather than by solvent distillation since the latter procedure would affect subsequent oil sorption of materials. This method gives an approximate oil sorption value. The sorbent with oil was squeezed between two rollers at 344.5 × 10^3 Pa (50 psi) before it was reweighed to determine the amount of recovered oil. The squeezed sorbent was again used in the sorption process. The efficiency of sorbent reusability was determined by oil sorption capacity of each sorbent after repeated sorption and desorption cycles.

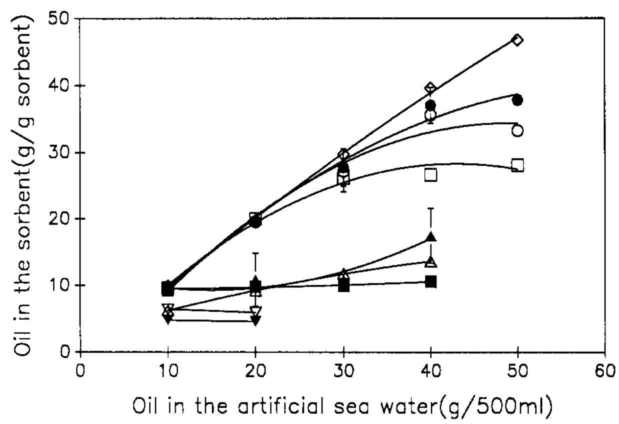

Figure 1. Light crude oil sorption. Key: O, COT; ■, PPW; ●, MW; ▽, KF; △, PP3; ▼, KC; ▲, PP15; ◇, MW (at 5 °C); □, MP.

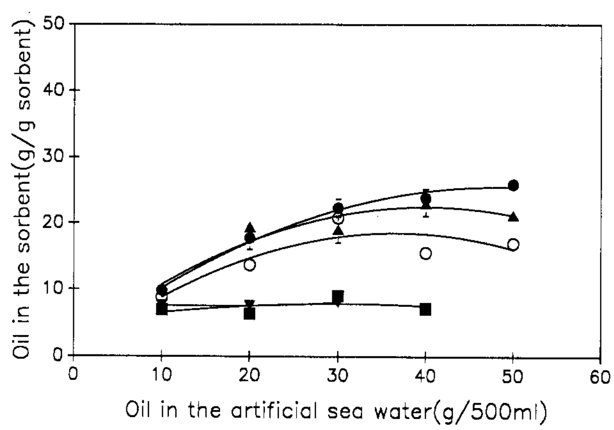

Figure 2. Bunker C oil sorption. Key: O, COT; ●, MW; ▲, PP15; ■, PPW; ▼, KC.

Results and Discussion

Sorption from Artificial Seawater. The oil sorption characteristics of different sorbents in the artificial seawater baths containing different amounts of oil are shown in Figures 1 and 2 for light crude oil and Bunker C oil, respectively. Even though it is not shown here, sorption trends of the sorbents with diesel oil are very similar to those of light crude oil due to the similar specific gravities of both oil samples. According to Johnson's results (*7*), oil sorbed on cotton increased with increasing specific gravity until it reached unity and then decreased. However, they did not explain why this phenomenon occurred. The specific gravity of Bunker C employed in this study was even higher than unity. Because of this high specific gravity, some portion of Bunker C oil, which was sunken in the seawater bath, made minimum contact with the sorbent during the sorption process. This contributed to the low sorption capacity of sorbents with Bunker C oil, with the exception of polypropylene fiber.

Among the sorbent materials examined in this research, milkweed floss showed the highest oil sorption capacity, followed by cotton fiber. One gram of milkweed floss can sorb ~40 g of light crude oil at room temperature. Unfortunately, the exact fineness of the fiber is not known, but observation by a light microscope revealed that milkweed fiber was coarser than cotton. The milkweed ranged in diameter from 20 to 50 μm while American upland cotton was approximately 25 μm (*14*). Therefore, the exceptionally high oil sorption by milkweed fiber can be explained by the large amount of wax on the fiber surface, ~3% compared with the 0.4–0.8% wax content of cotton, and the larger and noncollapsing lumen of the fiber, which gives more void volume for absorbed oil. The wall thickness of milkweed is only 10% of the total diameter of the fiber (*9*).

The oil sorption of milkweed was increased at 5 ± 2 °C, as shown in Figure 1. Increase of oil sorption at a low temperature was also observed in another study with other sorbents, which suggested that this increase was due to an increase in oil viscosity at this temperature (*7*). However, Schatzberg (*5*) pointed out that the rate of oil penetration into a capillary is inversely proportional to the oil viscosity and directly proportional to the capillary radius. It was also expected that a decrease in temperature should decrease the segmental mobility of the fiber, which would reduce the rate of absorption. At the initial stage of adsorption of oil onto the fiber surface, some interactions such as hydrophobic interaction and van der Waals force would occur between crude oil in the bath and wax in the natural sorbents. However, the absorption of oil within the fiber could be mainly influenced by the diffusion of oil through internal capillary movement, particularly for milkweed and cotton due to their lumens. Therefore, an increase in oil viscosity reduces the rate of absorption within the internal capillary movement of oil, but at same time it increases the adherence of oil onto the surface of the fiber and within the capillary during drainage. The experimental results of increase of oil sorption capacity with decrease in temperature, subsequently, and with increase in oil viscosity, implied that sorption time (10 min) was sufficient to minimize the effect of rate of absorption on oil sorption capacity of the sorbent. Extension of the sorption time to 30 and 60 min resulted in practically equal values in the oil sorption of milkweed floss. It was pointed out (*5*) that the oil sorption rates were very rapid so that the maximum capacity was nearly attained for most sorbents in 5 min. Furthermore, the results also suggested that at 5 ± 2 °C the decrease in segmental mobility of the fiber probably was not a significant effect in this case.

In comparison, 1 g of polypropylene fiber or polypropylene web only sorbed approximately 10 g of light crude oil. As expected, polypropylene fiber initially attracted large amounts of oil from the surface of the system because of its oleophilicity, but during the drainage, the fiber wad did not hold oil well so that large amounts of excess oil were drained. This phenomenon appeared to be more significant in light crude oil due to its low viscosity. Unlike other sorbent materials, the oil sorption capacity of polypropylene fiber (15 denier) was increased with Bunker C oil. Zahid et al. (*15*) claimed that the main mechanism in the oil sorption of polypropylene fiber was capillary bridges in the voids between the fibers rather than absorption or adsorption due to its high crystallinity. In this case, high viscous Bunker C would form a very coherent mass with polypropylene fiber so its oil sorption capacity should be increased. The fiber denier of the polypropylene fiber was considered one of factors in determining its oil sorption capacity (*7*). However, in the present study this effect was not clearly shown (Figure 1), presumably due to the considerable difference in crimping. The reduction in surface area with increase in fiber denier was compensated for by the effect of crimping, which, as described in the previous work (*7*), increased the accessible fiber surface area and, consequently, increased the oil sorption. In addition, since the staple length of 3-denier polypropylene fiber was extremely short, the geometry of the fiber wad was probably not favorable for oil adherence between fibers.

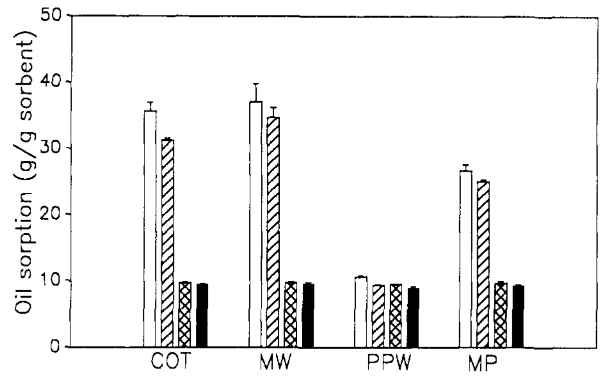

Figure 3. Oil sorption of water-soaked sorbents in the artificial seawater bath containing 10 and 40 g of light crude oil. Key: □, regular (40 g of oil); ▨, water soaked (40 g of oil); ▩, regular (10 g of oil); ■, water soaked (10 g of oil).

The nonwoven web made 60% milkweed with 40% polypropylene fiber resulted in oil sorption midway between the values obtained by milkweed floss and polypropylene web. Often sorbents are structured into sheets, booms, or pads, which are reusable and easier to control. In addition, the collection ability of these materials after application in an oil spill cleanup should be increased by making such structures. Since the introduction of milkweed in the web considerably increased the oil sorption capacity of polypropylene pad, the blending percentage should be further optimized in terms of their performance characteristics.

The oil sorption capacity of cotton fiber was lower than milkweed floss but still approximately 2.5–3 times higher than polypropylene web or fibers. Therefore, this study confirmed the previous result suggesting cotton fibers as potential sorbents for oil spill cleanup.

The oil sorption values of kenaf fiber and core materials were generally lower than that of milkweed or cotton but were similar to polypropylene web for heavy Bunker C oil. Kenaf fiber is much coarser than cotton and milkweed, and it occurs in a fiber bundle rather than a single fiber. Further separation of this fiber bundle to the single fibers should increase oil sorption comparably to polypropylene.

As seen in Figure 3, the presoaking of sorbent by water only slightly modified the oil sorption characteristics of sorbent materials with both 10 and 40 g of light crude oil in the bath. Since cotton, milkweed, and polypropylene are hydrophobic in nature, the water sorption during 10 min of soaking time was minimal.

Table III. Recovery of Oil and Reusability of Sorbents after Squeezing by Two Rollers[a]

fiber	first cycle: oil sorbed	first cycle: oil remaining[b]	second cycle: oil sorbed[c]	second cycle: oil remaining[b]	third cycle: oil sorbed[c]	third cycle: oil remaining[b]
			with Light Crude Oil[d]			
COT	33.2	1.5 (95)	27.9 (84)	1.3 (95)	24.5 (74)	1.2 (95)
MW	38.5	1.2 (97)	35.0 (91)	1.3 (96)	32.9 (85)	1.4 (96)
MP	26.8	1.8 (93)	24.6 (92)	1.7 (93)	24.1 (90)	1.7 (93)
PPW	11.3	1.7 (85)	9.4 (83)	1.6 (83)	9.4 (83)	1.6 (83)

[a] Units are gram of oil per gram of sorbent. [b] Values in parentheses represent percentage of recovered oil from the sorbent against the amount of oil sorbed in each cycle. [c] Values in parentheses represent percentage of sorbed oil against amount of oil sorbed in the first cycle. [d] Amount, 40 g/500 mL of artificial seawater.

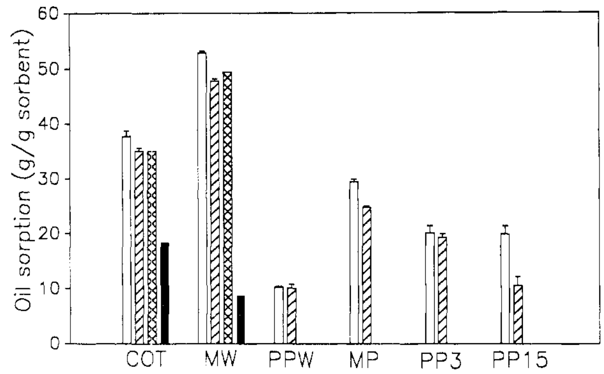

Figure 4. Oil sorption in the oil bath. Key: □, light crude; ▨, No. 2 fuel; ▩, No. 2 fuel extracted; ■, No 2 fuel scoured.

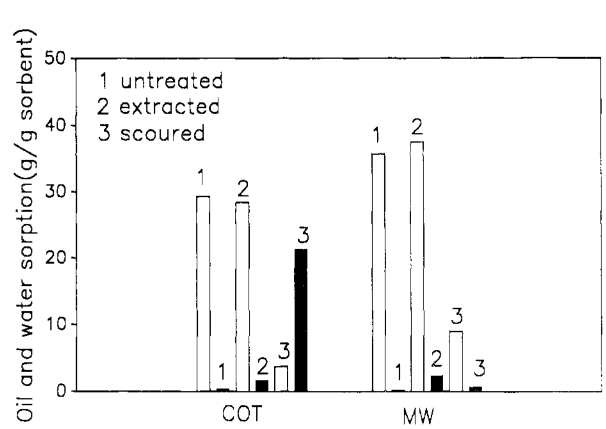

Figure 5. Oil sorption of extracted and scoured sorbents in the artificial seawater bath containing 40 g of diesel oil. Key: □, oil; ■, water.

Sorption without Water Medium. Often the sorbents are used to clean oil in the areas in which no water is involved. Since the sorption environment is different, oil sorption of sorbents is expected to be changed. In addition, this method would determine the maximum amount of oil sorbed by a particular sorbent. Figure 4 shows that oil sorption by the sorbent in the oil bath was slightly higher than the oil sorption in the artificial seawater bath containing 40 or 50 g of oil. The sorption of light crude oil by the sorbent was generally slightly higher than the sorption of diesel oil. Again, cotton and milkweed had considerable higher oil sorption capacities than polypropylene web and fiber. The nonwoven web of milkweed and polypropylene showed higher oil sorption than polypropylene web and fiber but lower sorption than cotton and milkweed. Therefore, it can be concluded that these natural sorbent materials should be suitable to remove oil not only from the surface of seawater, but also from places in which no water is involved.

Extracted and Scoured Sorbents. The Soxhlet extraction of cotton and milkweed fibers with 1,1,2-trichloroethane did not reduce their oil sorption capacities in diesel and light crude oil bath without artificial seawater (Figure 4) or in the artificial seawater bath containing 40 g of diesel oil (Figure 5). In the previous work (*7*), cotton fiber was extracted by a similar organic solvent (trichloroethylene), and there was only a marginal decrease in oil sorption capacity. It was not clear why the extracted fibers sorbed such high amounts of oil. According to Derry's result (*16*), immersion in trichloroethylene for 30 s reduced the wax content of an Indian grey cotton cloth from 1.09 to 0.15%. Therefore, it may be unreasonable to suspect the efficiency of Soxhlet extraction in removing surface waxes. A plausible explanation is that the fiber remained oleophilic due to residual organic solvents.

On the other hand, alkali-scouring treatment of cotton and milkweed significantly decreased their oil sorption capacities both in the pure oil bath (Figure 4) and in the artificial seawater bath containing oil (Figure 5). Both milkweed and cotton sorbed less than 10 g of diesel oil from an artificial seawater bath containing 40 g of diesel oil. As expected, water sorption by cotton was increased more than 10 times due to the removal of the natural wax coating making the fiber more hydrophilic. Alkali scouring of milkweed produced a hard, pulplike product, which resulted in less sorption of oil and water. However, even after the scouring treatment, cotton and milkweed sorbed 18.4 and 8.7 g of diesel oil from the pure oil bath, respectively, which is still comparable with values obtained for the polypropylene fiber.

Recovery of Oil and Reusability of Sorbents. Although more efficient means of recovering oil from the sorbent are available, compression of the sorbent is an economical and practical method. More than 90% of the sorbed oil was removed from the sorbents by a simple mechanical action, as given in Table III. The recovery of oil was decreased to 79–85% for the polypropylene web, suggesting stronger interactions between oil and polypropylene. If the contamination of the recovered oil is low, it can be recycled.

The sorbent is considered reusable if a loaded sorbent can be easily compressed or squeezed to its original size and shape (*2*). Even if there was a tendency toward decrease in sorbent efficiency with the repeated sorption and desorption, in the third sorption, milkweed and cotton fibers sorbed approximately 74–85% of the oil sorbed in the first sorption. For web samples, the oil sorption capacity tended to be slightly higher than fiber samples. These results suggest that, like polypropylene sorbent, cotton and milkweed sorbents can be recycled several times for oil spill cleanup with the aid of a suitable mechanical device.

Conclusion

We examined the oil sorption capacities of three natural fiber sorbents, milkweed, cotton, and kenaf, to determine their potential use in oil spill cleanup. Milkweed showed the highest oil sorption capacity followed by cotton fiber. The high oil sorption capacity of milkweed fiber was due to the large amount of wax on the fiber surface and the larger and noncollapsing lumen of the fiber. Both milkweed and cotton sorbed larger amounts of crude oil than polypropylene fiber and polypropylene web, which are commercially used as sorbents in oil spill cleanup. In general, the sorbents sorbed less of the heavy Bunker C oil than the other oil samples, with the exception of polypropylene fiber.

Solvent extraction and presoaking in water only slightly modified the oil sorption characteristics of the sorbents. On the other hand, an alkali-scouring treatment significantly reduced the oil sorption ability of the natural fiber sorbents. The majority of the sorbed oil was removed from the natural sorbents by a simple mechanical action, suggesting that the sorbents can be used repeatedly in oil spill cleanup.

The results suggested that a total or partial substitution of commercial synthetic oil sorbents, such as polypropylene, by natural sorbent materials, such as milkweed and cotton, could be beneficial in the oil spill cleanup operation by improving the efficiency of oil sorption and by incorporating other advantages such as biodegradability.

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