Utilization of silkworm cocoon waste as a sorbent for the removal of oil from water

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Abstract

The aim of this study is to investigate the utilization of silkworm cocoon waste, such as pierced or stained cocoons, as a sorbent material for the removal of motor and vegetable oils from water. The oil-sorption capacity, rate and reusability of the material were evaluated. The results show the high sorption capacity of the silkworm cocoon waste sorbent (42-52 $g_{oil}/g_{sorbent}$ for motor oil and 37- 60 $g_{oil}/g_{sorbent}$ for vegetable oil). The oil sorbed onto the material could be recovered by squeezing the sorbent, and the squeezed material showed an oil sorption capacity over 15 $g_{oil}/g_{sorbent}$. We concluded that the material shows a high performance as a low-cost and environmental friendly sorbent for the removal of oil from water.

Key words: silkworm cocoon waste, oil-sorbent

Introduction

The environmental pollution of water by oil has been a specific and serious problem (1,2). An oil spill in the environment causes adverse effects on wildlife and loss of oil, therefore, it is important to establish and develop techniques of oil removal from the water environment in order to apply the appropriate procedure to the cleanup of the oil pollution. The use of an oil sorbent is the commonly used technique to remove oil from the environment (3-8). Recently, the application of natural fibers, such as cotton (9), cotton grass fiber (10), milkweed, kenaf (11), vegetable fibers (12) and wool (13, 14), as the material for the removal of oil has been studied, and some of them showed higher oil sorption capacities for oil than the typical synthetic oil sorbent made of polypropylene. Natural oil sorbent fibers are environmentally friendly materials, because of their biodegradability and reusability. This feature makes natural fibers very attractive as oil sorbents compared to synthetic fibers.

In this study, we investigated the utilization of silkworm cocoon waste as a low cost sorbent for the removal of oil from water. In general, the silkworm cocoon is expensive. However, most of the pierced cocoons or very dirty cocoons of the silkworm are discarded as industrial wastes, and can be obtained as a low cost material. The silkworm cocoon has the property of a slow biodegradability (15), and the shell of the silkworm cocoon contains wax and shows hydrophobic property (16) which are important preconditions for an efficient oil sorbent (17). Based on these facts, there is the possibility that the silkworm cocoon waste acts as a high-performance material for the sorption of oil. The silkworm cocoon waste without removal of sericin was milled, and the obtained flocculate material (**Figure 1 b)**) was used as a sorbent for oil in this study. The oil-sorption capacity, rate and reusability of the silkworm cocoon waste sorbent (SCWS) were investigated.

Experimental

Sorbent material made of silkworm cocoon waste (SCWS)

The pierced silkworm cocoon of a commercial silkworm strain was used for the preparation of the SCWS. The pierced silkworm cocoons arise from the silk industry at the passage of the silkworm. The pierced cocoons of silkworms bred at Shinshu University were used (**Figure 1 a)**). The silkworm cocoon waste was dried according to the normal procedure using a cocoon drier (the temperature was programmed at 110˚C, then decreased to 60 ˚C at the rate of –0.14 ˚C /min.). The dried pierced silkworm cocoon was cut by scissors into small pieces (about 5 x 5 mm). The fractions were milled by a compact crusher (Force Mill, Osaka Chemical Co. Ltd., Osaka, Japan) for 1 minute. The obtained flocculate of silk fibers (**Figure 1 b)**) was used as a sorbent for the removal of oil from water.

For the evaluation of buoyancy of the sorbent, tests were performed by the method based on the procedure described in the literature[18]. Ten gram of the sorbent was placed in a basket containing a mesh bottom with 1 mm openings. Then, the basket was lowered into a dish filled with water to a depth of 8 cm for 15 minutes. At the end of the test, the buoyancy of the sorbent was observed.

Material

Motor oil (Toyota castle mineral oil SL-10W-30) was obtained from the Toyota Motor Corporation (Aichi, Japan). Vegetable oil (colza oil) was purchased from CGC Japan (Tokyo, Japan). It is a mixture of saturated (6%) and unsaturated (94%) fatty acids. The viscosities of the oils at 20°C were measured by a viscometer DV-II + Pro (Brookfield, Massachusetts, USA). The characteristics of the investigated oils are listed in **Table 1**. One gram of oils in petri dish were place for 24 hours and 10 days at room temperature. Then, the weight of oil loss was measured by an analytical balance. Sodium chloride was purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). The distilled water (pH= 7-8) was produced by an automatic water distillation apparatus (NANOpure II, Barnstead, Boston, Massachusetts, USA). Marine water was sampled at the offing of the Miura Peninsula in Japan. The salinity of the water was 29.2 %. Natural wool fiber was obtained from sheep (Suffolk) bred at Shinshu University.

Oil-sorption tests

For the sorption experiments, ten gram of the motor and vegetable oils were poured into a beaker containing 100 mL of distilled or marine water. Thereafter, 0.1 g of the SCWS was gently placed on the oil surface. After 10 minutes, the material was removed using forceps and drained for 1 minute. The material sorbed oil placed on a petri dish and then dried for 24 hours at room temperature (26-30 °C). The weight of the oil-sorbed material dried for 24 hours was not changed compared to that dried for 10 days at room temperature. Therefore, the period for drying was set for 24 hours. After drying, the oil-sorbed material was weighed by an analytical balance (0.001 g). Tests were carried out with and without stirring. In the case of stirring (dynamic system), the beakers were placed on a shaker (MK200D, Yamato, Tokyo, Japan).

The sorption capacity was determined according to the following equation:

$$q = (S_t - S_0) / S_0 \quad (1)$$

where q is the sorption capacity ($g_{oil}/g_{absorbant}$), S_t is the total mass of the sorbed samples (g) and S_0 is the initial mass of the sorbed materials.

For the reusability test of the material, ten grams of the motor and vegetable oils was poured into a beaker containing 100 mL of distilled water, and then 0.1 g of the SCWS was placed on the oil surface. Five cycles of the sorption process were performed for each sample. Between the each cycle, material was squeezed, and weighed. The recovery of oil was calculated by division of the difference between the oil-sorbed material and the material after squeezing by the initial quantity of the sorbed oil.

Results and Discussion

Removal of oil from water by SCWS

The sorbent material made of silkworm cocoon waste (SCWS) showed a water-repellent nature (**Figure 1 c)**), and floated on the water. The buoyancy tests showed, after 15 minutes in distilled and marine water, that the majority of the material remained at the surface of water and there was no much of settling of the sorbent under both static and dynamic conditions. By placing SCWS on the oil surface, the material sorbed oil and changed from a flocculent fiber to a gelatinous semisolid (**Figure 1 d)**). The results of the oil removal by the SCWS from distilled water containing 10 g of the motor and vegetable oil are shown in **Figure 2**. The sorption rate of the motor oil and the vegetable oil by the SCWS were not significantly different. The use of the sorption process over 10 min has no significant influence on the sorption of the oils, therefore, the sorption time was set at 10 minutes. The removal (%) of the motor oil and vegetable oil from distilled or marine water by the SCWS and the natural wool fiber are shown in **Table 2**. The material (0.1 g) removed over 50 % of the 10g of the oils on the water. On the other hand, the natural wool fiber removed less than 20 % of the 10 g of the oils in the water. The result showed that the higher performance of the SCWS as an oil sorbent compared to the natural wool fiber. In addition, the removal (%) of the oils from the marine water by the SCWS was the same level as in the case of the removal from distilled water. This result indicates that the SCWS could be used for oil removal not only from fresh water, but also from marine water. There was a tendency that the values of the oil removal (%) under dynamic system were lower than those under static system (Table 2, entry 1-8). The difference would be caused by the formation of slurry from a part of SCWS with oil.

Figure 3 shows the removal of oil from water vs. the weight of the silkworm cocoon waste. The 0.20 grams of the SCWS removed over 70 % of the 10 g of the oils added on the water. For the 10 g of added oils, the sorption capacities ($g_{oil}/g_{sorbent}$) vs. weight of the silkworm cocoon waste are shown in **Figure 4**. The sorption capacities of the SCWS were 42-52 $g_{oil}/g_{sorbent}$ for the motor oil and 37- 60 $g_{oil}/g_{sorbent}$ for the vegetable oil. Though we could not simply compare the performance of the SCWS as an oil sorbent to those of the other oil sorbent because of the difference in the used oil, the values of the oil capacities of the SCWS are higher than those of the other sorbent previously reported (**Table 3**). These results would be due to the high hydrophobicity and buoyancy of the SCWS.

Reusability of SCWS

The reusability of SCWS and the recovery of the sorbed oil are summarized in **Table 4**. The recoveries of the motor and vegetable oils were both over 90 %. The oil sorption capacities for the second cycle were approximately 40% of those for the first cycle with the values at the high levels of 22 and 18 $g_{oil}/g_{sorbent}$ for the motor and vegetable oils, respectively.

Further repeating of the sorption cycle (1-5 times) decreased the oil capacities of the SCWS (**Figure 5**). The decrease in the oil sorption of the SCWS by repeating the sorption treatment would be due to the decrease in the surface area of the SCWS by the aggregation of the oil between the fibers. Furthermore, there is a possibility that the denaturation of the surface protein of the SCWS by contact with the oil caused the decrease in the oil sorption capacity. However, after five sorption cycles, the sorption capacities were over 15 $g_{oil}/g_{sorbent}$.

In summary, the advantages of the SCWS as an oil-sorbent are as follows:

1) The preparation of the SCWS is very simple, and the material is low cost.
2) The SCWS has a slow biodegradable.
3) The SCWS has a high sorption capacity for oil because of the high hydrophobic property of the material.
4) The oil sorbed on the material could be recovered, and the SCWS material can be reused as an oil removal sorbent, which shows the sorption capacity over 15 $g_{oil}/g_{sorbent}$.

Based on these points, it is concluded that the SCWS is an effective and low cost sorbent for the removal of oil from water.

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Figure captions

Fig.1 Pictures of the silkworm cocoon waste sorbent. a) silkworm cocoon waste, b) sorbent made of silkworm cocoon waste (0.1 g), c) water and the silkworm cocoon waste sorbent, d) oil-sorbed material (motor oil) after drying for 24 hours at room temperature.

Fig.2 Oil-sorption rates of the silkworm cocoon waste sorbent (100mg). Oil-sorption rates are shown as the removal of oil from water (%) as a function of time in minutes. The quantity of the oils added on the water is 10 g. ○; Motor oil, ◆; Vegetable oil.

Fig.3 Removal of oil from water (%) vs. weight of the silkworm cocoon waste. The quantity of the oils added on the water is 10 g. The sorption time was 10 minutes. ○; Motor oil, ◆; Vegetable oil.

Fig.4 Sorption capacities ($g_{oil}/g_{sorbent}$) vs. weight of the silkworm cocoon waste. The quantity of the oils added on the water was 10 g. The sorption time was 10 minutes. ○; Motor oil, ◆; Vegetable oil.

Fig. 5 Reusability of silkworm cocoon waste sorbent for the removal of oil from water.

Table 1 Characteristics of the investigated oils

Sample	Viscosity[a] (cP)	Density (g/cm^3)	Weight loss (%) after 24 h
Motor oil	130	0.84	0.0
Vegetable oil	59	0.88	0.0

[a] The viscosities of oils at shear rate 13.05 s−1.

Table 2 Removal of motor oil and vegetable oil by silkworm cocoon waste and adsorbent cotton

Sorbent	Oil	Oil quantity (g)	Removal (%)	Standard deviation[b]
SWCW	Motor oil	1.5[a]	99	0.51
	Motor oil	10[a]	84	2.6
	Vegetable oil	1.5[a]	100	0.17
	Vegetable oil	10[a]	86	5.7
	Motor oil	10[c]	85	4.6
	Vegetable oil	10[c]	82	5.9
cotton	Motor oil	1.5[a]	30	12
	Vegetable oil	1.5[a]	14	6.5

[a] The amount of the used sorbent was 100mg. Oil was mixed with 100mL of distilled water. The sorption time was 10 minutes.

[b] n=3.

[c] Oil was mixed with 100mL of NaCl (3.5%) aqueous solution.

Table 3 Oil sorption capacity of various sorbents

Sorbent	Oil	Sorption capacity ($g_{oil}/g_{sorbent}$)	Reference
Natural wool fibers	Motor oil	33–43	13
Recycled wool-based nonwoven material	Motor oil	15–19	13
Sisal	Crude heavy oil	6.4	12
Leaves residue	Crude heavy oil	2.7	12
Saw dust	Crude heavy oil	6.4	12
Coir fiber	Crude heavy oil	5.4	12
Sponge gourd	Crude heavy oil	4.6	12
Silk-floss fiber (*Chorisia speciosa*)	Crude heavy oil	84.6	12
Silkworm cocoon waste	Motor oil	84–102	This study
Silkworm cocoon waste	Vegetable oil	68–86	This study
Absorbent cotton	Motor oil	4.5	This study
Absorbent cotton	Vegetable oil	2.2	This study

Table 4 Sorption capacity of the waste of silkworm cocoon for oils along two sorption cycles

Oil	Sorption capacity ($g_{oil}/g_{sorbent}$)[a]		The quantity of recovered oil (g)[c,d]
	First cycle	Second cycle	
Motor oil	84±2.6	66±3.4 (79)[b]	8.4±0.26 (100)
Vegetable oil	85±4.4	62±5.8 (73)	8.5±0.44 (100)

[a] The quantity of the sorbent (silkworm cocoon waste) was 100 mg. The sorption time was 10 min. Oil quantity was 10 g. Calculated according to the equation 1.
The values are the average and standard deviation (n=4).

[b] The values in parentheses are the percentage of the sorption capacity at the second cycle against it at the first cycle.

[c] The values are the quantity(g) of the oil obtained by squeezing the oil-sorbed material.

[d] The values in parentheses are the percentage of the quantity of the recovered oil against the quantity of the oil sorbed on the material.

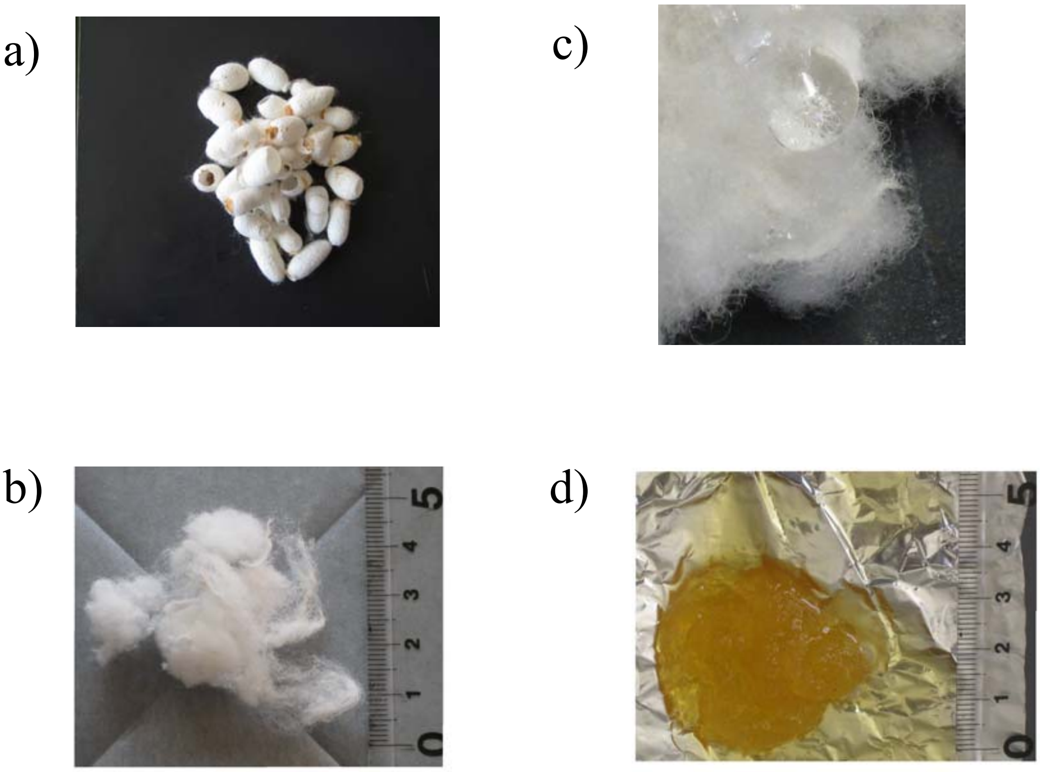

Fig.1

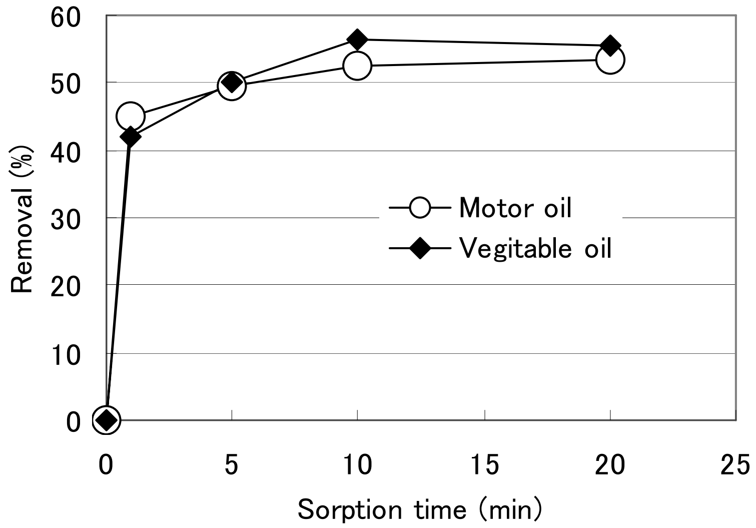
60
50
40
30
20
10
0
Removal (%)
Motor oil
Vegitable oil
0
5
10
15
20
25
Sorption time (min)

Fig.2

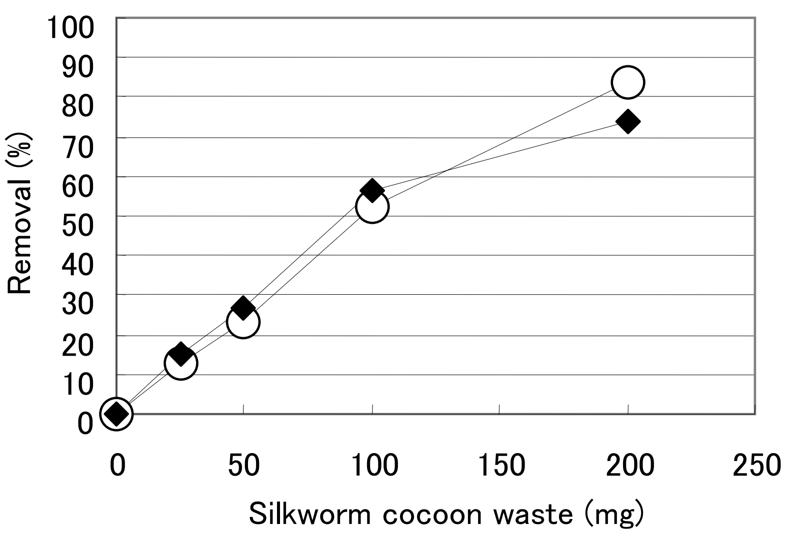
100
90
80
70
60
50
40
30
20
10
0
Removal (%)
0
50
100
150
200
250
Silkworm cocoon waste (mg)

Fig.3

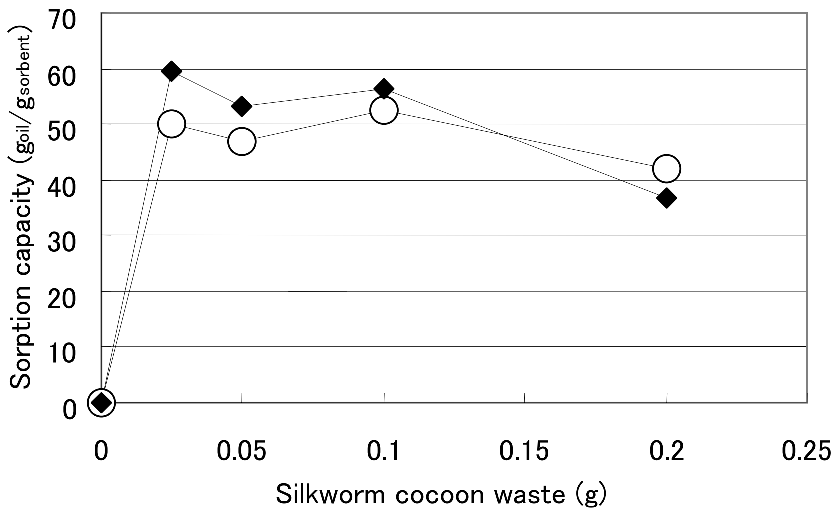
70
60
50
40
30
20
10
0
Sorption capacity ($g_{oil}/g_{sorbent}$)
0
0.05
0.1
0.15
0.2
0.25
Silkworm cocoon waste (g)

Fig.4

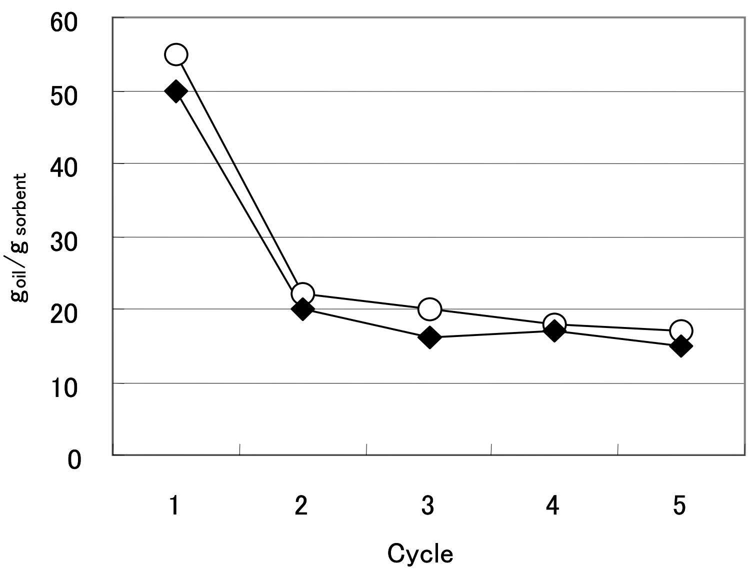
60
50
40
30
20
10
0
$g_{oil}/g_{sorbent}$
1
2
3
4
5
Cycle

Fig.5