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## Cleanup of water surface from oil spills using natural sorbent materials

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### Abstract

The following indicators were used to compare sorption efficiency of the test objects: oil capacity (OC), buoyancy, solubility of hydrocarbons in water, and water absorption (WA). Hereby, it was determined that the peat moss carbonized at the temperature of 200-250°C and modified by acetic acid has high sorption capacity. The sorbents introduced can increase the efficiency of water surface cleaning up until the water is almost clean and the residual oil content in water is less than 0.03 g/l.

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*Keywords:* Oil products; sorbent; oil capacity; water absorption; hydrophobization.

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### 1. Introduction

Production and refining of oil usually involves hydrocarbon emission, thus having negative impact on the environment and resulting in environmental disorder and ecosystem imbalance.

To mitigate potential consequences of oil spills, a series of ecological activities and cleanup operations including oil accumulation into the oil-spill boom (rough cleaning), as well as removal of the oil slicks with various sorbents

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are used. Among all of the oil spill cleanup methods that show good results in removal of oil from the water surface, sorbent cleaning-up is considered to be one of the most efficient<sup>1</sup>.

Nowadays, about two hundred of various sorbent materials are produced and used. Sorbents can be divided into some basic groups: inorganic, natural organic and organo-mineral, and synthetic.

Oil spill cleanup sorbents, in particularly, shall satisfy hard requirements taking into account their ability to take up oil but not water and to become quickly saturated by oil, being the most effective in recovering oil. Moreover, it should have and retain buoyancy, remaining afloat even when saturated with oil. When choosing sorbents for cleaning up spills, available oil recovery capacity of the sorbent and the oiled sorbent material disposal method shall be considered as well.

Special attention shall be paid to the natural fiber materials, straw, grain crops hull, flax processing wastes, sawdust, and peat that have been employed as sorbents. Cellulose as one of the important structural component of the plant materials is of special attention. One of the advanced natural sorbent material is peat moss (Sphagnum Dill); it is usually light green or varying in color from white to green and can be found in wet and boggy areas with poor soil. It forms a cushiony capitulum that floats on top of the water, being the top of the plant having living cells, and, at the same time, bottom part of the plant containing dead cells that form the peat. Tomsk region has about 30% (29 billion tons) of peat deposits. According to <sup>1</sup>, the average percentage and weight content of the principal organic components in the peat debris on a dry basis is from 3 to 10% of ashes, 45 to 85% of carbohydrates, 5 to 10% of proteins, and 5 to 10% of lipids.

Being a good adsorbent for hydrocarbons by its nature, Sphagnum moss has great moisture absorptivity; however, this ability is not so good when using the moss to clean up water surfaces.

Hydrophilic property of the sorbent allows water to be absorbed into the material structure, while oil to be kept on the surface of the sorbent material due to the adhesive force. A great variety and number of the active functional groups (COOH, OH and others) of the peat moss solid constituents (especially in humic substances) determine its high sorption and ion-exchange capacity. Peat bitumen is a hydrophobic constituent of the sorbent.

In nature, sphagnum has pH  $\approx$  4.5. Its acidity depends on the environment where it grows and availability of the humic acid in its cells, being natural by-product formed by biodegradation of dead plant matter. The above said sphagnum properties became a background to create simple, cost-effective, and environmentally friendly sorption-biological technology to clean up oil-contaminated water using sphagnum peat moss<sup>3,4</sup>

## 2. Experiment

*Oil capacity* (OC, g/g) and *water absorption* (WA, g/g) were determined following the methodology provided in the TU 214-10942238-03-95 technical specifications. Ability of the sorbents to absorb oil and water at the same time was assessed as follows: an oil slick of 0.5 to 5 mm in thickness was spread over the surface of the water (surface area is 48.50 cm<sup>2</sup>). The sorbent was distributed over the oil slick on the water surface, assuming 0.3 g per 10 cm<sup>2</sup>) and kept there for 6 or 96 hours. As the time passed, the peat moss was dewatered by filtering, and the adsorbed oil was extracted from the sorbent using carbon tetrachloride. Gravimetric method was used to determine the amount of the absorbed oil. IR spectroscopy method was used to estimate residual amount of oil in the water: a water sample was acidified to pH = 2 and extracted with carbon tetrachloride.

IR spectrum of the acidified water solution was obtained by measuring its absorbance (or optical density) at the wavenumber of 2.926 cm<sup>-1</sup>.

The oil product content ( $X$ ) in mg/l was defined according to the formula:

$$X = kD \cdot 100 \cdot 60 / LV \cdot 50 \quad (1)$$

where  $k$  is a coefficient, equal to 0.437 or 0.542;

$D$  is optical density;

10 is a volume of CCl<sub>4</sub> after dilution, ml;

6 is a volume of CCl<sub>4</sub> intended for extraction, ml;

$L$  is a depth of water in the liquid cell, cm;

$V$  is a volume of water taken to be analyzed, l;

50 is a volume of the aliquot part, ml.

*Sorbent buoyancy* was defined as follows: a sorbent charge with a weight of from 0.10 to 5 g was placed into the glass of 100 ml in volume filled in with water. The sorbent layer thickness in the glasses was from 1-2 to 5-7 mm. The sorbent residence time in water was 12, 24, and 36 hours (varied time). As the time passed, the sorbent afloat was taken out, dried in the drying oven at the temperature of  $103 \pm 1^\circ\text{C}$  during 2 hours. It had been drying till the constant weight; then, taking the weight difference, it was possible to determine the amount of the sorbent waterlogged and sunk.

*Water absorption.* Water absorption was defined according to the formula:

$$W = (M_1 - M) / M \cdot 100 \quad (2)$$

where  $W$  is water absorption, %;

$M_1$  is a weight of the sample taken out from water, g;

$M$  is a weight of the sample prior to be put into water, g.

### 3. Results and Discussion

This paper investigates oil adsorption processes using natural adsorbents of plant origin – a peat moss (Sphagnum Dill), grown in Russia, as well as Nature Corby and Spill-Sorb, manufactured in Canada.

The following indicators were used to compare sorption efficiency of the test objects: oil capacity (OC), buoyancy, solubility of hydrocarbons in water, and water absorption (WA).

Sphagnum Dill features with limited oil-absorbing capacity in comparison with the polypropylene fiber<sup>2</sup> but high buoyancy. However, one of the disadvantages of the sorbent is its high water absorption, resulted in loss of the sorbent buoyancy.

Hydrophobic materials are considered to be the most efficient adsorbents for organic compounds from water solutions, as their adsorption is mainly based on the dispersion force. Dispersion interaction of the organic molecules with carbonic structures of the hydrophobic adsorbent surface is much stronger than interaction of carbonic sorbents with the water molecules. Thus, the organic molecules are accumulated mostly on the boundary line between the adsorbent and water solution, being much more complicated multielectron system in comparison with the water molecules. Nevertheless, in practice, there is no any sorbent hydrophobicity phenomenon in natural surroundings.

According to the reasons, adsorbent hydrophobization was carried out by two methods. The first one is chemical modification of the cellulose included into the moss. A cellulose repeating unit has three hydroxyl groups.

Synthesis of the cellulose ester by etherification of its hydroxyl groups was carried out with acetic anhydride in the acid medium (15% of sulfuric acid upon the weight of the peat moss). In order to increase hydrolytic activity, the peat moss was preliminarily activated with the acetic acid vapors. The peat moss was acetylated at the temperature of  $80^\circ\text{C}$  for 5 hours, and then it was dewatered by filtering, flushed with water, and dried till the constant weight. Applying the sequential extraction method, carboxymethyl cellulose was extracted, and the results were analyzed. The absorption band appeared at  $1.730\text{ cm}^{-1}$  in the IR spectrum is the evidence of the acetate group presence, and, at the same time, reduction of the band intensity at  $3,400\text{ cm}^{-1}$  shows a hydroxyl group availability. Substitution value of the hydroxyl groups of 1.4 was determined according to the combined acetic acid content of 38%; therefore, etherification rate is 140. Increase of the sorbent hydrophobicity improves its buoyancy characteristics, as evidenced by the figures provided in Table 4.

The second method to increase the sorbent hydrophobicity is a heat treatment of the peat moss at the temperature from  $100$  to  $400^\circ\text{C}$ . A peat moss charge (4 g) is placed into the flask; the flask is closed to prevent the access of air to the carbonization zone. The time of burning at the steady-state temperature is 60 minutes, during which the flask with the peat moss inside the burner is turning around. Depending on the temperature, the peat moss changed its color from yellow to dark brown.

Coalification degree of the peat moss is defined according to the formula:

$$R = C_{\tau}/C_0 \cdot 100\% \quad (3)$$

where  $C_0$  and  $C_{\tau}$  are the weight of the peat moss before and after carbonization process, correspondingly. Difference between the coalification degrees was determined as follows:

$$\Delta R = 100\% - R \quad (4)$$

The results of calculation are combined in Table 1.

Table 1. Peat moss coalification degree

$T, ^\circ\text{C}$	$R, \%$	$\Delta R, \%$
100	92	8
150	91	9
250	85.2	14.8
300	38	62
350	25	75
400	14	86

In order to estimate adsorption activity of the peat moss, standard methodology of GOST 4453-74, applied when determining adsorption activity of the lightening powder charcoal, where the measure of activity is the amount of the methylene blue adsorbed from the solution by the charcoal charge, was used.

Methylene blue concentration in the solution before and after adsorption was determined using the Evolution-201 spectrophotometer. When the oil product concentration is within 20 and 150 mg/dm<sup>3</sup>, the majority of the oil products are in emulsion and colloidal forms. Molecularly-dispersed oil products contribution is insignificant because of low solubility of high-boiling oil in water. Oil product emulsibility in water depends on the content of the high-boiling components in the oil product such as tars, asphaltenes, and high-boiling waxes. Table 2 provides data on the adsorbing capacity of the test samples.

Table 2. Adsorbing capacity of sorbents

No.	Test sample	Adsorbed methylene blue, mg	Adsorption amount A, mg/g
1	Sphagnum Dill	22.50	90.02
2	Acetylated peat moss	18.50	74.00
3	Carbonized peat moss (200 °C)	19.20	76.80
4	Carbonized peat moss (250 °C)	24.95	99.80
5	Carbonized peat moss (300 °C)	20.85	83.40
6	Charcoal	35.00	140.00

It is evidently that the sorbent showing excellent results is charcoal, however, when using to clean up large water surfaces, it is not cost-effective. Nevertheless, one of the disadvantages of the charcoal is its poor buoyancy. In practice, charcoal of almost all types (92%) sinks in 30 minutes. The sorbent obtained by the low-temperature carbonization and the acetylated peat moss have the highest buoyancy.

Having porous structure, peat moss can actively absorb water that can be considered as its disadvantage when using to remove oil slicks. Water absorption by the sorbents was simulated in the laboratory environment matching the natural one. The sorbent was placed into the sample vial and, when constantly mixing, it was possible to define the height of the upper layer of the sorbent and the one having been sunk. Sedimentation velocity was determined according to the following ratio:

$$V_c = h_\tau / h_0 \quad (5)$$

where  $h_\tau$  is a layer of the sunk sorbent,  $h_0$  is a layer of the sorbent initially placed.

The obtained results are provided in Table 3. As it is evident from the table, the sedimentation velocity of the carbonized and modified peat moss within 170 hours is less by 43.57% and 13.4%, correspondingly, in comparison with Sphagnum.

Table 3. Sedimentation velocity of sorbents

No.	T, hours	V, %		
		Sphagnum	Modified peat moss	Carbonized peat moss
1	24	0.10	0.00	0.00
2	48	4.28	3.03	0.09
3	72	71.40	45.33	1.66
4	96	78.5	46.0	1.77
5	120	70.85	48.00	18.49
6	146	92.80	54.5	22.42
7	170	95.28	86.6	56.43

During carbonization and chemical modification, the peat moss is hydrophobized, thus, increasing its ability to absorb oil. Table 4 provides basic properties of the sorbents, showing that chemical modification and hydrophobization stimulate increasing of the adsorption activity of the sorbents, making them competitive with the peat mosses of the Nature Corby and Spill-Sorb types (Canada).

Table 4. Basic properties of sorbents

No.	Sorbent material	Oil capacity of sorbents, g/g	WA, g/g	Buoyancy, h
1	Nature Corby	12.5	1.13 – 1.25	48
2	Carbonized peat moss (250 °C)	14.2 - 15.7	1.3 – 1.5	146
3	Sphagnum Dill	5.8	3.1 – 4.2	96
4	Acetylated peat moss	7.60 - 8	1.8 – 2	120
5	Spill-Sorb	15.7	1.24 - .30	48
6	Charcoal	10.75	4.5-5.0	0.5

#### 4. Summary

Hereby, it was determined that the peat moss carbonized at the temperature of 200-250 °C and modified by acetic acid has high sorption capacity. The sorbents introduced can increase the efficiency of water surface cleaning up until the water is almost clean and the residual oil content in water is less than 0.03 g/l. As the calcification degree of the sorbent increases, its technical application characteristics improve. Further increasing of the calcification degree does not change the oil capacity of the sorbent.

The sorbents obtained feature with high buoyancy, oil capacity, and low sedimentation velocity. The sorbents are porous with rather developed cell structure allowing them to absorb the oil products well and retain them for a long time. Being a good adsorbent for hydrocarbons by its nature, Sphagnum moss exclude desorption probability, and thus, secondary contamination as well.

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