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Adsorption of hydrocarbons using natural adsorbents of plant origin

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Abstract

The paper investigates adsorption activity of natural sorbents to be used to clean up water surface from hydrocarbons under various temperatures. The natural adsorbents were compared by their oil capacity, buoyancy, and water absorption. It was revealed that *Nature sorb* (Canada) and *Sphagnum Dill* (Russia) natural sorbents demonstrate good buoyancy (up to 700 hours) and great oil capacity, and better sorption properties in comparison with the sawdust. The natural 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: adsorptive capacity; oil products; sorbent; oil capacity; water absorption; sawdust; hydrocarbons; sorbent disposal.

1. Introduction

Production, refining and transportation of hydrocarbons are inevitably accompanied by water pollution. Development of the offshore hydrocarbon production sites raises serious concerns about risks of environment pollution. The results of current oil spill response practices are not always as good as desired. Various methods can be used to clean up the water surface from oil slicks including mechanical, physicochemical, and biological. Oil in water can be of different states: bound, free, and soluble. Burning of oil spills results in additional air pollution with

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combustion products. Besides, the tendency of spilled oil to spread out in a thin film on the water surface makes burning difficult. When emulsifying detergents are used, oil is separated into fine particles.

Thus, the detergents do not remove oil from the water. Moreover, many of them are toxic substances that complicate degradation of hydrocarbons by hydrocarbon oxidizing microorganisms. Biodegradation of hydrocarbons is limited with ambient temperatures suitable for living of microorganisms. Thus, sorption technologies maintain leading positions worldwide. Various technologies to clean up oil-contaminated water were developed both for its static and dynamic conditions[1]. Sorbents that are used to eliminate oil spills from soil and water surfaces can be classified by various criteria: their purpose, disposal method, feedstock, wettability, buoyancy, and porosity[2].

Sorbents are divided into natural (peat, sawdust or straw) and synthetic ones, that have high oil capacity and relatively high cost.

Natural sorbents are characterized with limited oil capacity, good buoyancy, and low cost. Sorbent disposal method is a critical issue when selecting sorbent material. Natural sorbents are considered to be preferred in terms of this criterion. Advanced technologies allow cleaning up water from oil products using either powdered or low-ash coal. The coal is formed from the carbon-containing materials such as brown coal (lignite), the remains of dead vegetation, peat, and wood substance. High porosity coal is formed due to its activation using carbon dioxide, nitrogen, and alkali hydroxide[3-5]. However, this technology process is rather expensive, mainly, because of the sorbent cost and significant expenditures for the sorbent reactivation. Among the materials to clean water from the oil products are natural inorganic substances including anthracite culm, quartz sand, chemical chalk, randanite, opoka, tripolite, dolomite, zeolite, magnetite, and others[6, 7]. Their adsorbability can be increased by means of thermal and chemical activation[8, 9].

A lot of natural materials, such as sapropels, peat, and others, have rather good sorption properties. Moreover, the cost of natural sorbents is several tens of times lower in comparison with the synthetic sorbent cost, as they don't require their regeneration.

Systematic study of the natural material sorption properties when recovering oil of various types from water was introduced in the referenced papers 10 and 11. In order to enhance decontamination of oil-polluted water, the authors developed combined multi-layer sorbents that allow removing oil substances of various degree of dispersion from water with purification efficiency of up to 92-98%. Due to high hydrophobic nature, porous synthetic materials adsorb oil products very efficiently. Polypropylene, foam plastics, oxidized atactic polypropylene, and carbamide foam plastics belong to porous synthetic materials. In this respect, fibrous composite materials filled with polymeric matrix and vegetation residues are of great interest. Thus, it makes the cost of sorbent reduced and its disposal much easier[12].

Nowadays, the investigations to produce cheaper sorption materials containing industrial by-products and agricultural residues are carried out[13].

The sorbents based on cellulose stand out from other natural sorbents[15-17].

On average, softwood contains 48-56% of cellulose, 26-30% of lignin and 23-26% of hemicellulose (10-12% of pentosans and 13% of hexosans). Hardwood has slightly different composition: 46-48% of cellulose, 19-28% of lignin and 26-35% of hemicellulose (23-29% of pentosans and 3-6% of hexosans). The structures of moss and peat depend on proportions of cellulose (48-85%), proteins (5-10%) and minerals. The content of lipids (5-10%) contributes to hydrophobicity properties of moss and peat. Lignin is considered to be a major constituent of natural fibers. Besides, the sorbent structures depend on the presence of undecomposed plant remains, which form peat, decomposition products, and inorganic substances. Peat has outstanding porosity that depends on its decomposition level, and consequently, on availability of humic acid and lipids. Refer to the referenced paper 18, oil absorbent was offered to be obtained by means of cellulose fiber treatment using 1,2-polydiene[18]. As a result, the obtained material shows good hydrophobicity with the oil capacity of 25 g/g. Thus, one of the main objectives to develop water cleaning-up technologies is to obtain natural sorbent materials that don't require any complicated preliminary preparation.

This paper investigates hydrocarbon adsorption using natural sorbents.

The test objects included Sphagnum Dill – Russian peat moss, Nature sorb – Canadian sphagnum peat moss, charcoal and sawdust in different fineness. The following three indicators were used to compare sorption efficiency of the test objects: oil capacity, water absorption, and buoyancy.

2. Experiment

Adsorbing capacity was determined by the methodology provided in the referenced paper 13. Decolorisation properties were determined according to the amount of methylene blue dye adsorbed from the solution, and adsorptive capacity according to the change of iodine concentration in the solution. Methylene blue and iodine concentrations in the solution before and after adsorption were determined using photoelectric surface colorimetric and Evolution-201 spectrophotometer.

Adsorption amount was defined as follows:

$$A = \frac{a}{m} \quad (1)$$

where

a is a weight of methylene blue adsorbed by the adsorbent charge, mg;

m is a weight of absolutely dry adsorbent, g.

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 water surface (surface area is of 48.50 cm^2). The sorbent was distributed over the oil slick on the water surface, assuming 0.3 g per 10 cm^2 and kept there for 6 or 96 hours. As the time passed, the sorbent 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 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[4] (or optical density) at the wavenumber of 2,926 cm^{-1}.

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

$$X = kD \cdot 100 \cdot 60 / LV \cdot 50 \quad (2)$$

where

k is a coefficient equal to 0.542;

D is optical density;

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

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

Thin-layer chromatography method was used to estimate residual amount of oil in the water.

Calibration and calculation. The spot area (mm^2) corresponding to 100 μg of hydrocarbons (F) is established experimentally. For this purpose, a standard solution of nonvolatile hydrocarbons (petroleum oil) in carbon tetrachloride with the concentration of 5 mg/ml (or 5 μg/μl) is prepared. The standard solution is used for calibration. It is used to measure spots corresponding to 20 and 10 μl portions of the solution. The difference between the areas of these spots corresponds to 80 μl portion of the standard solution, and thus, containing 400 μg of hydrocarbons.

Water absorption. Gravimetric method was used to determine water absorption (*W*):

$$W = (M1 - M)/M^{*}\ 100 \quad (3)$$

where

%; 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

Oil is a mixture of hydrophobic hydrocarbons. Solubility of oil products in water or water in oil is negligible. Mixing and turbulent flow of fluids result in emulsifying and complicate separation of water and oil. The following processes of oil products removal are used depending on the sorbent structure: physical surface sorption that is defined by the quantity of specific surface and oil products kept by a sorbent due to the effects of capillary forces. Table 1 provides the data on the adsorptive capacity of the sorbents. The highest adsorptive capacity was observed for charcoal studied at the initial concentration of methylene blue and iodine of 160 mg/l.

Table 1. Adsorptive capacity of sorbents

Sorbent properties	*Sawdust*	*Nature sorb*	*Sphagnum*	*Peat*	*Charcoal*
Decolorisation according to adsorbed methylene blue dye, mg/g	18-20	43-46	37-40	20-24	200-230
Adsorptive capacity according to iodine concentration, %	25.3	58.5	57.7	55.2	60.0

Nature sorb moss is only slightly different from Sphagnum Dill moss grown in Siberia.

The sorbents were sorted by size using 0.5 mm, 1 mm and 1.4 mm sieves to increase their adsorbing capacity and surface-volume ratio. Adsorptive capacity was determined in the same manner. The results are detailed in Table 2.

Table 2. Accumulation of methylene blue in sorbents depending on their particles size

D mm	1.4 mm	1.0 mm	0.5 mm	Mixture
Nature sorb, mg/g	48-50	45-58	50-56	55-64
Sawdust, mg/g	18-20	20-22	24-28	20-22
Sphagnum, mg/g	24-26	37-40	45-50	30-32

However, sorbents with small pore diameter are difficult to apply on the water surface. They become easily movable in windy conditions and have poor buoyancy.

The following indicators were used to compare sorption efficiency of natural adsorbents of plant origin: oil capacity, buoyancy, solubility and water absorption. The obtained results are provided in Table 3.

Table 3. Basic sorbent properties

No.	Sorbent material	Oil capacity of sorbents, g/g	Buoyancy, h
1	Nature Corby	11.5	over 720
2	Charcoal	12.7	48
3	Sphagnum Dill	5.8-8	600-700
4	Sawdust	1-3	200-250

It is evident that charcoal is an excellent sorbent material showing best oil absorption results. However, it has poor buoyancy. Oil contamination of water involves interaction of abiotic environmental factors: petroleum composition which is subject to continuous change (dilution, evaporation) and abiotic environmental factors affecting the ecosystem (temperature, humidity, pressure). To evaluate basic petroleum composition properties it was necessary to consider the contents of light end, cyclic hydrocarbons and tars. Therefore, model mixtures of hydrocarbons and lube oils were prepared to estimate the influence of these factors.

Sorbents under test were used to absorb oil spills from water surfaces over extended ranges of ambient and water temperatures: +10 ºC, 0 ºC. Hydrocarbons viscosity changes at the abovementioned temperatures, and thus, adsorptive capacity will depend on the temperature[4] (see Table 4).

The majority of oil products spilled in water is in emulsion and colloidal forms. Oil product emulsability in water depends on the content of the high-boiling components in the oil product. These compounds form the basis of oil cuts.

Table 4. Oil capacity of *Sphagnum Dill* (g/g of adsorbent) depending on temperature

Hydrocarbon	Viscosity, η, 10^{-3} Pa·s 0 ºC	Viscosity, η, 10^{-3} Pa·s +10 ºC	OC, 0 ºC	OC, +10 ºC
Octane	0.710	0.618	4.86	5.34
Pentane	0.278	0.254	6.84	8.0
Gasoline	0.73	0.52	5.46	6.04
Benzene	-	0.65	5.82	5.97
Toluene	0.771	0.668	5.05	5.87
Kerosene	2.2	1.5	6.0	6.2
Oil	1,100	987	9.73	8.96

It was determined that oil capacity is a function of such variables as density, molecular weight, temperature, and viscosity. Motor oils and oil residual are absorbed by any sorbent. This is because of micelles are covered with a colloid film that appears during adsorption of hydrocarbons on a sorbent when oil emulsion is formed. The film consists of diffuse layers of hydrophilic colloids making emulsion stable and absorbable by any sorbent. *Sphagnum Dill* and *Nature Corby* mosses featuring with high buoyancy suppresses evaporation of light hydrocarbons for a sufficiently long period of time ensuring safety for individual working in oil spill areas. The inherent capillary action of peat and mosses provides a wicking action that absorbs and encapsulates hydrocarbons. The cellular structure of the Sphagnum family features two types of cells: chlorophylls, involved in photosynthesis, and hyaline cells. Hyaline cells are porous and their structure is strengthened by fibrils. Consequently, peat and moss have higher adsorptive capacity in comparison with sawdust.

4. Summary

Hereby, it was determined that Sphagnum Dill and Nature Corby mosses have high sorption capacity, good buoyancy and low sedimentation velocity. The sorbents introduced can increase the efficiency of water surface cleaning up until the residual oil content in water being less than 0.03 g/l.

The main advantage of natural sorbents is their safety to the environment. Having been used, the adsorbents completely degrade over time and do not require special disposal. Sawdust carbonized at the temperature of 150-250 °C should be used for highly viscous oil products.

Due to high buoyancy and adsorption rate, sorbents can be easily collected from water surface and incinerated as fuel bricks.

Tomsk region has substantial potential resources of sawdust and moss. The sorbents are low-cost and therefore, should be of practical use.

References

1. F.Berne, I. Gordonier Wastewater purification. French Institute of Petroleum. *Editions techne*. Paris: 1997.
2. S.A. Sayeda, A.M. Zayedb. Investigation of the effectiveness of some adsorbent materials in oil spill clean-ups. *Desalination* 2006; 194**:** 90-100.
3. Alcaniz-Monge J., Linares-Solano A., and Rand B. Water adsorption n activated carbons: study of water adsorption in micro- and mesopores. *J. Phys. Chem*. 2001; **B. 105:** 7998-8006.
4. Bandosz T., Biggs M.J., Gubbins K.E., et al. Molecular models for porous carbons. *Chem. Phys. Carbon* 2003; **28:** 41-228.

5. Macia-Agullo J.A., Moore B.C., Cazorla-Amoros D., and Linares-Solano A. Activation of coal tar pitch carbon fibers physical activation vs. chemical activation. *Carbon* 2004; **42:** 1367-70.
6. Oya A. and Kasahara N. Preparation of thin carbon fibers from phenolformaldegid polymer micro-beads dispersed in polyethylene matrix. *Carbon* 2000; **38:** 1141-4.
7. Wingenfelder U., Furrer G., Schulin R. Sorption of antimonite by HDTMA-modified zealots. *Micropor. Mesopor. Mat.* 2006; **95**: 265–271.
8. Xu H., Yang L., Wang P., Liu Y. Kinetic research on the sorption of aqueous lead by synthetic carbonate hydroxyapatite. *J. Environ. Manage.* 2008; **8:** 319–328.
9. Tyagi B., Chudasama C., Jasra R. Characterization of surface acidity of an acid montmorillonite activated with hydrothermal, ultrasonic and microwave techniques. *Applied Clay Science* 2006; **31:** 16–28.
10. Jimenez de Haro M.C., Perez-Rodriguezт J.L., Poyato J. Effect of ultrasound on preparation of porous materials from vermiculite. *Applied Clay Science* 2005; **30:** 11–20.
11. Wang Y., Lin F., Pang W. Ammonium exchange in aqueous solution Using Chinese natural clinoptilolite and modified zeolite. *J. Hazard. Matter* 2007; **142:** 160– 4.
12. Kutchin A., Shubnitcina E., Sazonov M, Demin V. Protection of ground and water areas with use natural adsorbents. *London: Thomas Telford* 2000; 2**:** 1486 p.
13. Azizian S., Haerifar M., Bashiri H. Adsorption of methyl violet onto granular activated carbon: Equilibrium, kinetics and modeling. *Chem. Eng. J.* 2009; **146:** 36–41.
14. New chemical technologist handbook «Feed stocks and products of organic and inorganic industries». Part 2 – Saint-Petersburg: *Mir & Seamy Publishing Group* 2002; 1142 p.
15. Clemenson Lyle J. Environmental Filtration, Ins. Method of processing peat for use in contaminated water treatment. Gfn. 6042743 CIF 03.08.1998.
16. Bilkey Peter C. A Research International, Ins. Water-and oil-absorbent medium comprising milled sphagnum, sphagnum moss. And/or sphagnum peat. Pat. 6890651 USA 11.04.2003.
17. Toyoda Masahiro, Inagaki Michio, *Carbon*, 2000; **38:** 199.
18. Pat.21512250. RU, 2000.