

MODIFICATION OF NATURAL PETROLEUM ADSORBENT SPHAGNUM DILL

Olga V. Rotar^{1}, Victor G. Rotar¹, Tatyana A. Gess¹, Alexander A. Iskrizhitsky², Daniel S. Vorobiev³*

¹ *Institute of Natural Resources, Tomsk Polytechnic University, Russia*

² *TomskNIPIneft, Russia*

³ *Tomsk State University, Russia*

Received September 9, 2016; Accepted November 2, 2016

Abstract

Adsorption activity of natural adsorbents for cleanup of water surfaces from oil spills was studied. The following natural adsorbents criteria were compared: oil absorption, buoyancy, and water absorption. The original peat moss Sphagnum Dill (Russia) demonstrated better buoyancy (up to 700 hours) but poorer oil absorption in comparison to Nature sorb (Canada). Carbonized and chemically modified Sphagnum Dill was found to be similar to Canadian peat mosses Nature Corby and Spilcorb in terms of oil absorption and superior to them in terms of buoyancy. Modified adsorbents can clean water to the residual oil content of less than 0.03 g/L. Adsorptive capacity demonstrated dependence on adsorbent porosity.

Keywords: adsorptive capacity; oil products, sorbent; oil capacity; water absorption; sawdust; hydrocarbons; sorbent disposal.

1. Introduction

Oil, consisting of a mixture of aromatic and aliphatic hydrocarbons, does not dissolve in water due to its hydrophobic properties, thus presents an environmental problem in the case of emergency oil spills during oil transportation and refining because it degrades slower than water-soluble compounds.

There is a number of different ways to clean water from oil using physical separation method. Detergents are used to dissolve oil structure and thus make oil partially soluble in water. These surface-active agents create water-soluble micelles with petroleum nucleus and the surface of detergent. This method also damages the environment since the majority of used chemicals are toxic. The basic method to respond problems related to oil spills is sorption [1-3]. When choosing an adsorbent, it is necessary to consider not only its basic characteristics such as oil absorption, water absorption, and buoyancy but also the methods of used adsorbent disposal. Low-ash coals modified with nitrogen and carbon dioxide to increase their porosity are used as adsorbents to clean water under statistical conditions [4-6]. To respond oil spills, adsorbents shall be both oleophilic and hydrophobic. Inorganic adsorbents have higher hydrophobicity: anthracite chips, zeolites, sand and chalk [6-8]. Synthetic fiber materials, such as polyethylene, polypropylene, and atactic oxidized polypropylene, are good adsorbents of hydrocarbons. To reduce adsorbent cost and facilitate its disposal process plant, wastes are included in the polymer matrix as a filling material [9]. The adsorbents which combine lyophilic and hydrophobic behavior are cellulose containing materials being able to participate in ion-exchange reactions [10-11]. Adsorbent efficiency depends on the amount of cellulose in the material, cellulose crystallinity, specific surface area and degree of polymerization. Together with regions of a high degree of order (crystalline regions), there are amorphous regions with a low degree of order. The content of crystalline regions in wood with a cellulose content of 48-56% is less than in cotton. The presence of hydrophobic components (lignin, bitumen, pectins, and waxes)

provides adsorbents with water repellency. The paper [11] demonstrates that adsorption is determined by composition, structure, and proportion of components. Natural adsorbents despite their diversity are characterized with high water absorption capacity and relatively low oil absorption capacity in comparison with polymer and inorganic adsorbents. The exception is Nature Corby, Spilcorb adsorbent made in Canada and obtained according to the specification provided in [12]. The basic approach to increase adsorbent hydrophobicity is to modify cellulose containing adsorbents by treating them with chemicals: sodium hydroxide [13], Fenton's reagent [14], organic acids and acid amides [15-16], carbonization [17].

This paper studies target-specific modification of peat moss (Sphagnum) and the following three properties of the modified material: water absorption capacity, oil absorption capacity and buoyancy.

2. Experimental

Oil absorption (OA, g/g) and water absorption (WA, g/g): an oil slick of 0.5 to 5 mm thick was created over water surface in a drum with a cross-section area of 250 cm. The sorbent was distributed over the oil slick. As the time passed, the sorbent was dewatered by filtering, and the adsorbed oil was extracted from the sorbent using carbon tetrachloride. The gravimetric method was used to determine the amount of the absorbed oil. The residual amount of oil in the water was determined with an IR spectroscopy method at the wave-number of $2,926\text{ cm}^{-1}$ and a thin-layer chromatography method.

A gravimetric method evaluating weight difference of the original adsorbent (M) and the water saturated adsorbent (M_1) was used to determine water absorption ($W\%$):

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

Peat moss carbonization

A peat moss charge (4 g) was placed into a flask; the flask was closed to prevent the access of air into carbonization zone. The time of burning at the steady-state temperature from 100 to 400°C was 60 minutes. Coalification degree of the peat moss was defined according to the formula: $R = C_t/C_0 \cdot 100\%$, where C_0 and C_t are the weights of peat moss before and after carbonization process respectively. The difference between coalification degrees was determined as follows: $\Delta R = 100\% - R$.

Treatment with sodium hydroxide

Peat moss was bathed in 0.5% sodium hydroxide solution and kept at room temperature for 24 hours. Then, it was filtered by flushing in a filter with water until a neutral medium and dried at the temperature of 100°C.

Adsorbent freezing

The pre-damped adsorbent was frozen at the temperature of -18°C during three days and then it was defrozen and dried at the temperature of 100°C.

3. Results and discussion

Study objects included natural adsorbents of plant origin: peat moss Sphagnum Dill (Russia), Nature Corby and Spilcorb (Canada), and peat. The following basic criteria were used to compare adsorption of the study objects: oil absorption, buoyancy, and water absorption.

Adsorption activity was determined by the amount of methylene blue dye (MB) adsorbed on sorbent from the solution. Accumulation of MB by adsorbents is presented in Tab. 1.

It was found that peat moss has twice higher adsorption capacity than peat but 5-6 times lower than activated charcoals. The main disadvantage of using peat moss for cleaning water surfaces is its high moisture absorptivity.

The adsorbent hydrophilic property allows water to easily fill in amorphous regions in cellulose structure, generating hydrogen bonds with hydroxyl and carboxyl groups and resulting in adsorbent swelling and reduces its oil adsorption capacity as well as buoyancy. Oil is absorbed by adsorbent surface due to physical sorption „sorbent-sorbate“. When an adsorbent comes into contact with oil, it creates molecular interaction resulting in disruption or generation of new chemical bonds. This interaction determines the creation of hydrogen bonds

and the van der Waals forces. Water kept in pores of an adsorbent by capillary forces fills in capillary pores with the diameter of 1 mm minimum.

Table 1. Adsorption capacity of sorbents for methylene blue at time

Study object	Adsorbed MB, mg/g	
	60 s	180 s
Sphagnum Dill	37.70	40.0
Sphagnum Dill (100°C)	43.50	54.20
Sphagnum Dill (200°C)	45.1	56.10
Sphagnum Dill (250°C)	47.67	58.54
Sphagnum Dill (300°C)	67.87	70-85
Activated charcoal	35.00	200-230
Sphagnum Dill acetate	51.08	61.40
Peat	20-24	39.60

Hydrophobic materials are considered to be the most efficient adsorbents for organic compounds from water solutions, as their adsorption based mainly on the dispersion force. Nevertheless, in practice, there is no any sorbent hydrophobicity phenomenon in natural surroundings.

Moss hydrophobization involved chemical modification of 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 synthesis was performed at the temperature of 80-100°C during 5 hours. In IR spectrum an absorption band appeared at 1,730 cm⁻¹ corresponding to a carboxyl group. Combined acetic acid content was 38-50%.

The second method to increase sorbent hydrophobicity is heat treatment of peat moss at the temperatures from 100 to 300°C. Moss carbonization results in disruption of chemical bonds in polysaccharides, intermolecular bonds between cellulose and hemicellulose, and a decrease of capillary water in moss structure. Depending on the temperature, the peat moss changed its color from yellow to dark brown. The carbonized moss has higher adsorption capacity as evidenced by the accumulation of MB in the adsorbent.

The main criteria for using an adsorbent to clean water surfaces in nature are its water absorption capacity and buoyancy. Dependence of adsorbent sedimentation velocity decreases significantly with the increase of carbonization temperature. The sorbents treated at the temperature of 250-300°C have the highest buoyancy. Sedimentation velocity was defined according to the formula (Tab. 2):

$$Vc = h_{\tau} / h_0$$

where h_{τ} is a sunk adsorbent layer; h_0 is an original adsorbent layer.

Table 2. Dependence of sedimentation velocity (Vc) of Sphagnum Dill (SphD) and Sphagnum Dill (300°C) on different particle sizes at time

T, hours	Vc , (mesh-0.14)		Vc , (mesh-0.5)		Vc , (mesh-1)		Vc (mesh-1.4)	
	SphD	SphD (300°C)	SphD	SphD (300°C)	SphD	SphD (300°C)	SphD	SphD (300°C)
1	0.10	0.01	0.10	0.03	0.10	0.070	0.11	0.070
2	0.10	0.01	0.11	0.03	0.12	0.070	0.13	0.070
3	0.10	0.013	0.11	0.03	0.13	0.070	0.13	0.080
4	0.10	0.014	0.13	0.04	0.14	0.075	0.18	0.085
5	0.11	0.014	0.13	0.04	0.15	0.075	0.18	0.090

The adsorption capacity of sorbents depends on the size of particles, with decreasing of it the size of specific surface increases and so does adsorption capacity. Adsorbents were milled and screened on meshes of different pore sizes. Molecular interconnections disrupt during milling and hydroxyl groups release. Table 2 provides data on adsorbent sedimentation velocity.

With decreasing of adsorbent particle size, the size of specific surface increases and spatial capillary structure reduces, and thereby sedimentation velocity slows down. Water absorption defined according to the abovementioned formula increases with increasing of adsorbent particle size.

The cellular structure of moss consists of two types of cells: chlorophyllose cells involved in photosynthesis and large empty hyaline cells strengthened with fibrils, cells can absorb 20 times more water than the dry dead weight of the plant. Water is eliminated and replaced with air during carbonization. Thus, dried sphagnum plants maintain cell structure and therefore adsorption capacity in Tab. 3. Oil absorption, OA (g/g), was determined to evaluate the maximum amount of adsorbed hydrocarbons.

Table 3. Dependence of water absorption and oil absorption of Sphagnum Dill (300°C) on particle size

D, mm	0.14	0.5	1	1.4
W, %	0.67	0.94	1.430	1.560
OA, g/g	15.10	14.40	14.23	13.90

Waxlike substances with hydrophobic properties escape to the surface during drying of moss. Due to that, moss capacity to absorb oil and hydrocarbons increases and at the same time oil recovery decreases, and also oil adsorption capacity of carbonized moss decreases with mesh size reduction.

When a dry sphagnum moss contacts oil, it absorbs oil quickly and retains it well due to the presence of barriers in hyaline cells. Adsorption capacity of different types of moss and synthetic polypropylene (PP) fiber [18] sorbent is compared in Tab. 4.

Table 4. Sorbent properties

Sorbent material	OA, g/g	WA, g/g	Buoyancy, h
PP fiber (21030-16)	4-9.4	0.05	-
Spilcorb (Canada)	3.96-8	1.6 - 2.0	48
Sphagnum Dill (original)	5.8	3.1 - 4.2	96
Acetylated peat moss	7.60-8	1.8-2	120
Carbonized peat moss (200°C)	8.23-9	1.5-1.7	170
Carbonized peat moss (300°C)	14.2-15.7	1.3-1.5	146
Activated charcoal	10.75	4.5-5.0	48

Treatment of moss, peat, and sawdust with 0.5% alkali solution results in a change of their structure and proportion of components. As a result, lignin, waxes, and humic acids are eliminated, and cellulose crystallinity is reduced thus increasing porosity. This results in an increase of adsorptive capacity to MB, but material hydrophobicity decreases leading to reduced oil absorption capacity of adsorbents.

Adsorbent modification by freezing was found to be more efficient. At low temperatures moisture fills in pores that result in the generation of ice crystals in sorbent structure during freezing and thus wedging of pores. Defreezing followed by drying results in disruption of cellular walls and thus facilitates the increase of the amount of pores and sorbing surface.

The original Sphagnum Dill features limited oil absorbing capacity in comparison with polypropylene fiber. However, one of the disadvantages of the sorbent is its water absorption resulting in loss of sorbent buoyancy.

4. Conclusions

1. Carbonized Sphagnum Dill was found to be similar to Canadian peat mosses Nature Corby and Spilcorb in terms of oil absorption and superior to them in terms of buoyancy.
2. Hydrophobic materials are considered to be the most efficient adsorbents for organic compounds from water solutions, as their adsorption based mainly on the dispersion force. In comparison with the original moss, carbonized and acetylated peat mosses feature high oil absorption capacity, low water absorption, and higher buoyancy. Oil and water adsorptive capacities of sorbents were found to be dependent on their porosity

References

- [1] Rotar OV, Rotar VG, Iskrizhitsky AA, Sharipov ZI, Pimenova AA. J. Procedia Chemistry. 2014; 10, 145-150.
- [2] Berne F I. Gordonier Eputation dese annx residuares de raffinage, Ed. Technip, Institut Francais du petrole et des Moteurs: Paris, 1997; Vol. 3, Cnapter 1; p. 89.
- [3] Sayeda SA, Zayedb, AM. J. Desalination. June 2006; Vol. 194, Issues 1– 3, 90-100.
- [4] Alcaniz-Monge J, Linares-Solano A, Rand B. J. Phys. Chtm. 2001; B. 105, 7998-8006.
- [5] Bandosz T, Biggs MJ, Gubbins KE, et al.: J. Chem. Phys. Carbon. 2003; 28, 41-228.
- [6] Macia-Agullo JA, Moore BC, Cazorla-Amoros D, Linares-Solano A. J. Carbon. 2004; 42, 1367-1370.
- [7] Oya A, Kasahara N.:J. Carbon. 2000; 38, 1141-1144.
- [8] Wingenfelder U, Furrer G, Schulin R. J. Micropor. Mesopor. Mat. 2006; Vol. 95, 265-271.
- [9] Kutchin A, Shubnitsina E, Sazonov M, Demin V. Protection of ground and water areas with use natural adsorbents, Ed.; Thomas Telford: London, 2000; – Vol. 2, p.1486.
- [10] Laszlo JA, Dintzis FR. J. Appl. Polym. Sci. 1994; Vol. 52, 531-538.
- [11] Young RA, Rowell RM. Cellulose structure modification and hydrolysis, Ed.; Wiley-Interscience: 1986; p.379.
- [12] Bilkey Peter C. U.S. Patent 6 890 651, 2003.
- [13] Gurgel LVA, Karnitz O Jr, Gi, RPF, Gil LF. J. Bioresour. Technol. 2008; Vol. 99, (8). 3770-3783.
- [14] Argun ME, Dursun S, Karatas MM. J. Bioresour. Technol. 2008; Vol. 99 (18), 8691-8698.
- [15] Abdel-Aal SR, Gad Y, Dessouk, AM. J. Appl. Polym. Sci. 2006; Vol. 99, 2460-2469.
- [16] Bao-Xiu, Z., Peng, W., Tong, Z., Chun-Yun, C., Jing S.: J. Appl. Polym. Sci. 2006; Vol. 99, 2951-2956.
- [17] Xu H, Yang L, Wang P, Liu Y. J. Environ. Manage. 2008; Vol. 86, 319-328.
- [18] Bordunov VV, Bordunov SV, Leonenko VV. J.Ecology and Industry of Russia. 2005; Vol 8, 8-11.

Corresponding author, address: Institute of Natural Resources, Tomsk Polytechnic University, 30, Lenin Avenue, Tomsk, 634050, Russia; tel.: (+7-3822) 606120; fax: (+7-3822) 563-435; e-mail: rotarov@tpu.ru