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# Oil spill cleanup of water surface by plant-based sorbents: Russian practices

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ABSTRACT

The paper analyses the best practices of Russian researchers, including the authors of the article, in the field of crude oil and refined products cleanup of water surfaces by alternative sorbents. Sorption methods and using low-cost plant based sorbents are emphasized. Various modification methods (heat treatment, chemical modification, etc.) of the above mentioned sorbents are discussed, which are aimed at increasing oil sorption capacity and developing hydrophobic properties. It is evident from the review that these sorbents have considerable potential for the oil spill cleanup.



## 1. Introduction

Currently, considerable experience is gained for responding to oil spills on water areas. In a number of cases, preference is given to using sorbents due to their advantages, viz. the potential for purification of severe oil pollution, attaining a high degree of purification, recycling and repeated regeneration of used sorption materials, etc.

## 2. Current oil spill cleanup sorbents

In the Russian Federation, a wide variety of materials are used as sorbents. These include inorganic natural sorbents (sand, loam, etc.) and man-made sorbents (perlite, expanded clay, silica gel, etc.), organo-mineral materials (sapropels, slades, caustobiolith), organic materials (peat, coal peat, graphite, etc.); synthetic materials (polypropene, polyethylene, polyurethane, phenol formaldehyde foams, etc.); natural organic sorbents based on animal raw materials (wool, flocks, etc.) and plant raw and waste materials (moss, foliage, straw, husk from grain processing, waste paper).

Despite a low sorption capacity (from 3 to 5 kg/kg or more), a low cost of plant-based sorbents and renewable annual supply of raw materials draw the attention of specialists.

Sorption capacities of different sorbents applied for oil spill cleanup in the Russian Federation are listed in Table 1.

The Russian market of industrial sorbents is advancing rapidly, in recent decades the range of sold sorbents has increased from 2 to 30 to several hundreds, and research aimed at developing more effective and cheaper products is constantly being conducted.

## 3. Using plant wastes as sorbents

The choice of any waste as a commercial sorbent is conditioned by its physical and mechanical and sorption properties,

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**Table 1 – Sorption capacities of different sorbents.**

| Sorbent | Sorption capacity kg/kg |
|---|---|
| Activated carbon AU-3 (all-union state standard 20464-75) | 4.5–10 |
| Macropore technical carbon | 4–4.5 |
| Peat sorbent *Sorboyl S8* | 8–10 |
| Lessorb-extra | 8 |
| Phenol formaldehyde resin (powder) | 4.42 |
| Uremiks-913 | 25 |
| Peat sorb | 4–6 |
| Sawdust | 4.5–8.5 |
| Fallen leaves | 8–9 |
| Waste of grass processing | 4–6.5 |
| Peat | 8–10 |
| Rice husk | 6–10 |
| Cotton felt | 6–30 |
| Hemp rope | 10–13 |
| Sunflower husk | 6–8 |
| Waste paper | 8–9.5 |
| Corncobs | 5–7 |
| Wheat straw (shreddings) | 4.1 |
| Flax shive | 5–10 |
| Knop (flocks) | 8–13 |

as well as the potential for its changing. Thus, the main requirement imposed on such materials is a highly developed porous structure with hydrophobic surface area (high surface area to volume ratio, including external and available internal surfaces). A cost factor is another key issue. Therefore, sorbents obtained from plant and animal wastes are one of the most attractive targets.

A number of authors propose to use plant wastes untreated. Thus, they offer to use dried corncobs, rye and wheat bran, millet and buckwheat husks, etc. in mixture with sawdust as a sorbent for the purification of oil-contaminated objects (Garaev, 2008). There are a number of works where unconditioned grains of wheat, corn, oats, and other crops (Glumov et al., 1998; Zemnukhova et al., 2005; Glumov, 1998; Zemnukhova, 2005; Sobgaida et al., 2009) are suggested to be used as sorbents.

The research of some authors (Khlestkin and Samoylov, 2000; Yagafarova et al., 2002; Baltrenas et al., 2004; Shaikhiev et al., 2010; Stepanova et al., 2010) reveals that wastes of cotton processing are good sorbents of crude oil and oil products. Thus, it has been argued that to clean up the water surface polluted by oil it is sufficient to apply the required material in an amount of 5–10% of the oil weight. In addition, it is currently reported that wastes from cotton processing factories containing textile fluff and impurities emulsified by loom oil have sorption capacity from 5 to 40 kg/kg for a wide range of oil products.

Furthermore, some researchers (Kablov et al., 2000; Nikitina et al., 2008) suggest to use composition plates from fine cut fibrous cellulosic material (fine cut dried grass, fine cut straw, etc.), rubber crumb and polyethylene powder to clean up the water surface from oil and oil products.

It is known that lignin and cellulose are the main components of plant wastes, which define their hydrophilic characteristics. Consequently, besides sorbing oil and oil products quickly and well, these sorbents also absorb moisture which has a negative impact on cleanup efficiency as water occupies a part of interstitial space. In reference with the above, at the present time many studies are focused on the improvement of hydrophobic characteristics and the development of the porous structure of sorbents.

### 3.1. *Coal and activated carbon from plant wastes*

Heat treatment or carbonization of plant-based materials is one of the common ways of modification as it contributes to the development of porous structure. Carbon, produced by carbonization of natural plant material, preserves its sophisticated initial structure. By changing conditions of carbonization, it is possible to get complex compositions of carbon with other materials (Kuznetsov, 1990; Harry and Francisco, 2006).

Gafarov et al. (2004, 2005) proposed a sorbent preparation method which consists in the heat treatment of the silicon–carbon raw material (rice and buckwheat husks) at a temperature of 200–430 °C. The effectiveness of cleanup from oil by this sorbent was 98%.

It is interesting to note that number of authors research materials based on heat-treated rice husks, which have certain peculiarity in comparison with other agricultural wastes. In its structure the material contains organosilicon compoundings, which transform into carbon and silicone dioxide over carbonization and provides additional hydrophobic characteristics and enforced structure. So, Zemnukhova et al. investigated the possibility of using rice and buckwheat husk for water's purification from emulsified and dissolved oil products, but the effectiveness of purifying was not so high. In the future, these scientists proposed a method of sorbent preparation by pyrolysis of rice husks fraction form up to 3 mm at a temperature of 350–500 °C (Zemnukhova and Khohryakov, 2005).

Nevertheless, using other carbonized biomass material for oil spill cleanup is also effective. The authors of studies (Sobgaida et al., 2011) developed a method of obtaining sorbent from the wheat husk, heat-treated at a temperature of 250–300 °C, and from cotton-fluff heat-treated at a temperature of 350–400 °C. The obtained product revealed high efficiency for the water purification from oil and oil products.

Besides, the high cleanup efficiency of heat-treated sugar mud is determined (Sverguzova and Blagadyreva, 2008). The heat treatment of sugar mud leads to imperfect combustion of organic impurities, As a result of this, the carbon particles are formed. A sorbent (Kireicheva et al., 2003) containing a carbonized flax shive and sapropel is suggested. The authors of the study (Utkina et al., 2011) showed the potential of obtaining sorbents from different fine cut plant raw materials (reed, sawdust) by special heat treatment and further modification.

In the practice of water purification, an activated carbon having high hydrophobicity is used more frequently than other adsorbents. The process of obtaining activated carbon of high quality is time-consuming and complicated, so its cost is sufficiently high, it leads to its multiple uses. A number of authors (Ivahnyuk et al., 1997; Dolgih and Ovcharov, 2008) suggest obtaining activated carbon using waste from processing plant raw materials after the preliminary fermentation. In particular, the method of sorbent production from straw and reed chaff with the addition of food and paper industry wastes is suggested.

The potential to obtain activated carbon from sunflower husks by its carbonization at a temperature of 350 °C for 30 min in nitrogen flow is also known. The method implies obtaining activated carbon without using a short cut binding agent. This sorbent is proposed to be used for the cleanup of marine oil spills by means of pneumatic, hydraulic-mechanical or manual sieving followed by gathering of floating saturated oil-sorbent aggregates.