

Technological recommendations for the use of leaf litter based adsorption material to remove an oil slick from water bodies surface

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Abstract. The paper presents the study results on properties of leaf litter based adsorption material. The indicators of mixed leaf litter, characterizing it as an adsorption material, are established. Measurement of samples wetting angle with oil and water showed that the original material has hydrophobic properties. The oil intensity was about 10 g/g, and water absorption was 5-6 g/g, in addition, moisture, ash, total pore volume, bulk density were determined. Degree of water purification from oil was more than 98%, and biotest of purified water showed a decrease in toxicity 2.5 times. Based on this, technical options, are proposed for using mixed leaf litter for accidental oil spills response on the water surface with the help of mats, booms and universal design booms. Thermal combustion is proposed as a method of spent adsorption material disposal.

1. Introduction

The increase in production and transportation, refining and consumption of oil and its derivatives lead to a global environmental degradation. Oil and its derivative products adversely affect all links of the biological chain.

One ton of spilled oil pollutes almost 12 km² of water surface. Oil prevents oxygen from entering the water, which leads to the loss of a water body properties as a full-fledged favorable environment component. Oil slicks can significantly disrupt exchange of energy, heat, moisture, gases between the ocean and the atmosphere. The cessation of aeration can be detrimental to all living organisms in the pond.

Oil-containing waters are divided into two different groups: the first is the waters of natural reservoirs contaminated as a result of accidental and unauthorized discharges of oil products, and surface runoff from urban and industrial sites, seaports, etc.; the second is wastewater generated as a result of technological processes at oil production, storage, processing and transportation facilities, washing of any type of transport, etc. [1].

Cleaning the water bodies surface from contamination involves removing an oil slick by mechanical and (or) physico-chemical methods. The most promising and environmentally sound way is considered to be a method of removing oil slick products using oil sorbents [2].

The literature describes numerous methods for producing sorbents and filtering materials for water purification from oil products and technological schemes for their application. Presently, the sorbents are imposed with a number of maximum versatility requirements. First of all, this is high oil absorption, then environmental safety, buoyancy and minimal water absorption [3]. The development and study of sorption materials that would meet these requirements and have a low price is an urgent task.

A variety of raw materials are used for production of sorbents [4-10]. The most promising sorbents are production and consumption waste, as it allows to simultaneously solve a disposal problem. In particular, trees leaf litter collected in recreational city areas can be used as adsorption material. This waste cannot be used as basis for mineral fertilizers and compost, since pollutants (car wastes, ben-



zopyrene, anti-icing agents, etc.) penetrate the stomata, are fixed in the leaves, and can enter the plant root system, causing its death, in addition, they contribute to biological pollution of soils. Therefore, it is to be disposed in urban landfills. Use of plant polymer waste in order to obtain new materials is an important task [11]. Presently, there are many technological methods for processing plant polymer waste into composite materials [12]. Using the material to clean the water surface from oil spills would solve two environmental problems at once: production of cheap adsorbent and reducing the negative impact on ecological systems.

The aim of the work is to study the processes of oil removal from water surface by the leaf litter based adsorption material and development of technological recommendations for its use in the accidental oil spills response.

2. Materials and Methods

2.1. A subsection

Model water contaminated with oil slick was the objects of the study for the work.

The high-sulfur Devonian oil of the Tumutukskiy field was considered as a pollutant.

The mixed leaf litter of trees collected from recreational zones in city of Kazan (Russia) was used as sorption material. The collected material was dried at a temperature of $20 \pm 5^\circ\text{C}$ and ground to particles with a size not exceeding 10 mm². The average composition of mixed leaf litter: birch - 34-29%, poplar - 31-28%, linden - 10-9%, maple - 10-8%, others - 15-14%.

2.2. Methods for Determining Main Sorption Characteristics

Defining main characteristics, which are total pore volume, poured density, ash content, moisture, buoyancy of the samples, was carried out according to standard methods [13, 14].

Sorption capacity for iodine: a sample of sorption material weighing 10g was previously boiled for 10 minutes in 200 cm³ 0.2 N. HCl solution, then it was washed with distilled water and dried for 1 hour at a temperature of 100-110°C. To determine 1g of the material, it was shaken for 15-30 minutes with 100 cm³ of 0.1 N solution of iodine in KI (25 g/dm³), then a 10 cm³ sample was titrated with 0.1 N solution of sodium thiosulfate (indicator is starch). Iodine value was determined by the formula:

$$E_1 = 12,7 \cdot (V_1 - V_2) / m_y, \quad (1)$$

where, V_1 and V_2 are volume of 0.1 N sodium thiosulfate solution before and after addition of sorption material;

m_y is the mass of the sample (g).

Sorption capacity for oil under static conditions: 50 dm³ of Devonian oil was poured, and a 40 mm × 40 mm × 10 mm brass mesh box was placed into petrie dishes, in which there was a test sample weighing 1g. After 1, 5, 15, 30, 45, and 60 minutes, the brass box with the test material was removed, some of the oil was drained, and the mass of the sample was determined on an HR-200AZ laboratory balance. The experiment was carried out at an ambient temperature of $20 \pm 5^\circ\text{C}$.

Static oil intensity was determined by the following relation:

$$A = m_{\text{absorb}} / m_{\text{sorption}}, \quad (2)$$

where, m_{absorb} is the mass of absorbed oil (g);

m_{sorption} is the mass of sorption material (g).

For the experimental determination of water absorption by mixed leaf litter, a sample weighing 1g was put in 40 mm × 40 mm × 10 mm brass mesh box, which was placed on the water surface. After 1, 5, 15, 30, 45, 60 minutes, the box with the test sample was removed, excess water drained, and it was weighed on HR-200AZ laboratory balance [13].

Water absorption was determined by the following ratio:

$$B = m_{\text{absorb}} / m_{\text{sorption}}, \quad (3)$$

where, m_{absorb} is the mass of absorbed oil (g);
 $m_{sorption}$ is the mass of sorption material (g);
 B is water absorption (%).

The residual oil content in the water was determined by the extraction method. The contents of the petrie dishes (oil-contaminated water) were poured into the separatory funnel, and 6 cm³ of extractant, which was CCl₄, and 1 ml of 0.1 N HCl solution were added. The contents were shaken vigorously three times for 10 minutes, and settled until its complete stratification into extract (CCl₄ + oil) and refined water. The separated extract layer, previously passed through an ashless filter, was placed in a crucible. When the contents of the crucible were heated, CCl₄ was evaporated. The residual oil content was determined by the difference in the mass of the crucible before and after extraction.

2.3. Instrumental Methods

For visual observation of the oil absorption process (spreading on the surface, absorption), and samples of the materials before and after sorption, Micromed R-1 microscope with a dcm 130 video eyepiece was used. 100x magnification photographs were taken with use of the proposed software.

Biotesting is a procedure for determining environmental toxicity with the use of test objects that signal danger, regardless of what kind and combination substances cause changes in vital functions of the test objects. The biotesting was carried out in a accredited analytical test center laboratory of Kazan (Volga region) Federal University. The test procedure was carried out in accordance with Federal Registry.1.39.2007.03222 and Federal Environmental Regulation 14.1: 2: 4.12-06. *Daphnia magna* Straus was used as a test object; observation duration was 48 hours.

The determination of chemical elements (in mass fractions) in the ash produced after burning the spent oil-saturated sorption material was carried out in a SUR-02 “Renom FV” spectrometer (a universal X-ray spectrometer CYP-02 «Реном ФВ»), using an X-ray fluorescence method. The working wavelength is 0.001-2 nm.

3. Results

3.1 Main Characteristics of Leaf Litter as a Sorption Material.

Table 1 demonstrates values of the total pore volume, poured density, ash content, moisture, buoyancy and sorption capacity of the materials under study towards iodine.

Sorption activity largely depends on the moisture content of a sorbent. The moisture content of mixed leaf litter was 8-10%, that indicates no need in additional heat treatment. This moisture value will not affect the oil absorption from water surface.

The ash content of the sorption material shows how much sorption material remains after complete thermal burning. Low ash content can significantly simplify the process of spent sorption material disposal.

The value of the total pore volume of an adsorbent for water gives an idea of the maximum volume of a substance which this adsorbent can absorb. This indicator is quite high (table 1) for mixed leaf litter, while for mineral sorbents it is at the level of 0.5-2 cm³/g.

Table 1. Main Characteristics of the Mixed Leaf Litter.

Parameter	Unit of Measurement	Mixed Leaf Litter
Moisture	%	10.01
Ash Content	%	0.21
Total Pore Volume for Water	cm ³ /g	7.58
Poured Density	g/cm ³	0.08
Sorption Capacity for Iodine	%	27.80
Buoyancy for 24 h	%	92.00
Buoyancy for 72 h	%	69.70

To determine the presence and quantity of micropores in the sorbent, the iodine sorption capacity was determined. The experimental data shows that mixed leaf litter has a highly developed surface that combines various types of pores.

The buoyancy values of the samples indicate that the studied adsorption material is technologically applicable and can stay on the water surface during sorption process without any additional holding devices.

The main indicator of any adsorption material is its ability to absorb a specific pollutant. In the case of an oil spill response, the leaf litter has not only to absorb the oil, but also has to be hydrophobic, because under favorable weather conditions (air and water temperatures are above 20°C), oil can spread over the water surface as a thin slick [14]. If the oil slick thickness is less than 3 mm, the leaf litter is in direct contact with water. If the material is hydrophilic, the pores will be filled with water, which will cause decrease in buoyancy and the adsorption capacity of the samples towards oil. Figure 1 shows that the sorption capacity for oil with a contact time of 5 to 60 minutes for mixed leaf litter is more than 10 g/g, which is averagely 60% higher than the sorption capacity for water. Thus, the material is sufficiently hydrophobic. To conduct an experiment on measuring the leaf litter sorption capacity, imitation of an oil spot was created: oil was put on water ($V = 7$ ml) so that the thickness of the spot was 5-7 mm, while the sorption capacity of the material for oil decreased slightly. Obviously, this is due to the incomplete filling of pores with oil.

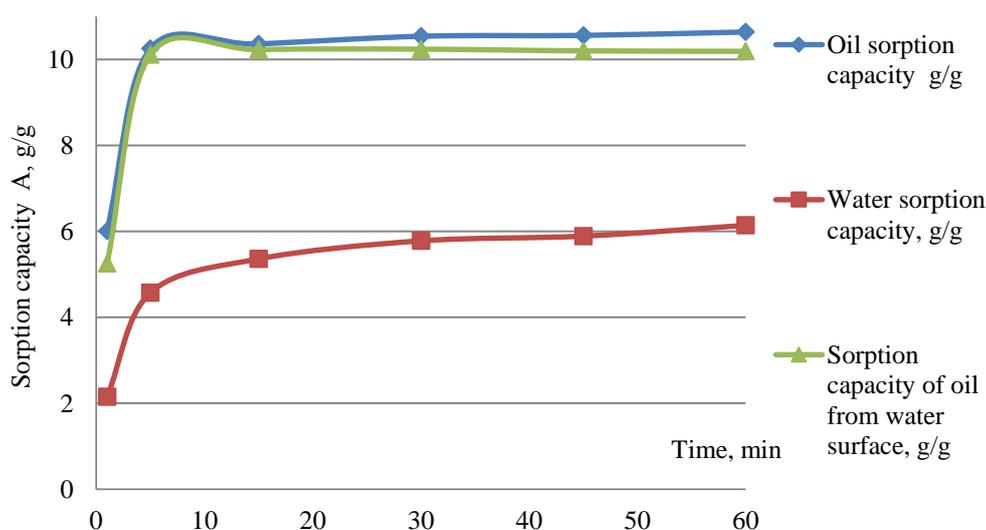


Figure 1. Sorption capacity of mixed leaf litter for oil, water, and oil from water surface.

Analyzing of these dependences let us conclude that oil absorption from the water surface is uneven. With increasing holding time, the samples capacity increases and their full saturation occurs after 30 minutes. It is explained by filling of the samples pores with water and oil, and the equality of rate values of the sorption and desorption processes. When sorption material is put on a contaminated surface, contact with oil occurs first. The components included in oil wet the leaf litter surface more actively, than water and the pores are filled with contaminants.

Figure 2 demonstrates photographs of leaf litter samples before and after oil sorption taken with Micromed R-1 (Микромед Р-1) microscope. Since the main part of the mixed leaf litter contains birch and poplar leaves, these samples were examined under a microscope in particular.

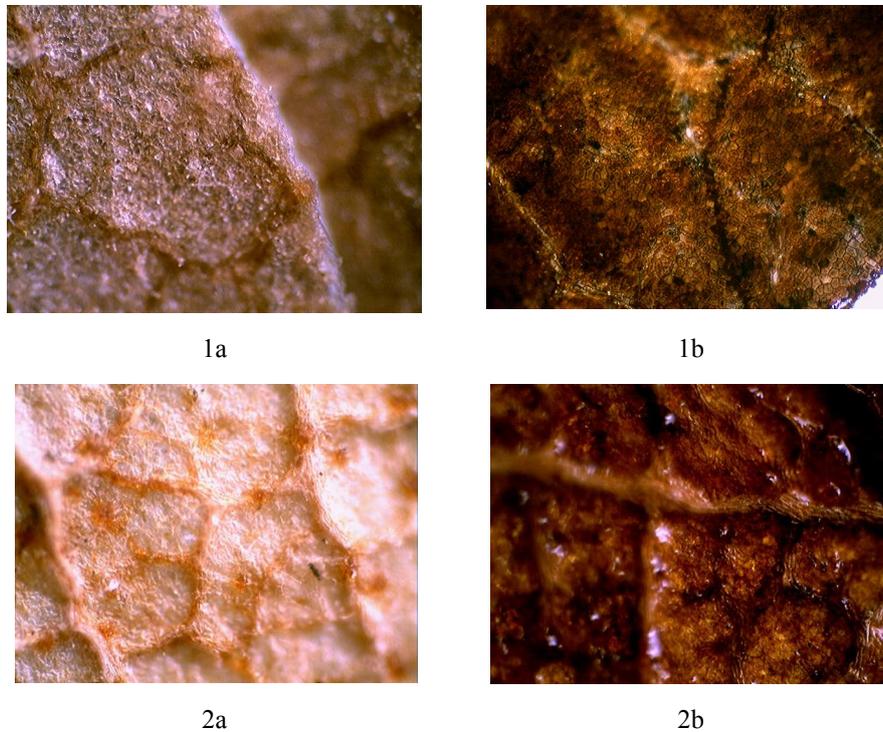


Figure 2. Microphotographs of leaves samples 1 – birch leaf litter, 2 – poplar leaf litter (a – original, b – covered with oil slick).

The micrographs demonstrate that the oil not only adheres to the surface of the leaf litter, but also goes deep into some areas, as evidenced by darker spots in the tubules of the leaf. Therefore, the leaf litter can be considered as a plant adsorbent.

For a more detailed study of the interaction of leaf litter with water, the hydrophobicity of the original and oil-wetted samples was determined by measuring the wetting angle. Figure 3 shows time dependences of changes in wetting angle of the original and oil-wet samples.

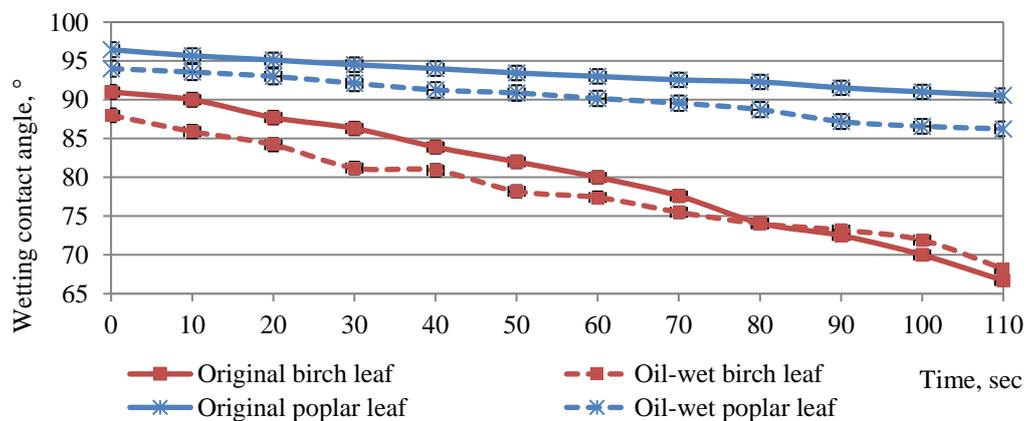


Figure 3. Dynamics of the original and oil-wet samples' surfaces wettability by a distilled water drop.

The difference between the original and oil-wet samples is insignificant. Lower contact angles (4-5°) of the wetted samples indicate that, when the leaves contact with oil and water, oil is absorbed first, forming a slick on the surface of the material, which prevents filling pores with water, and oil fills all the pores. This can be explained by the lower oil density, due to which the adsorbate rate of diffusion in the interport space is higher than that of denser water. The presented results can be confirmed by the fact that the leaf surface has a more pronounced affinity for oil than for water.

After removing the oil slick from the water surface, the residual oil content in the water was determined by the extraction method. It is possible to calculate the purification degree of polluted water from oil using the known residual concentration. The purification degree (CO, %) shows the fraction of the substance absolute amount that is captured by the sorbent and gives a fairly complete picture of the process nature. This indicator is an important criterion in determining optimal conditions of the adsorption process and is calculated by the following formula:

$$CO = \frac{C_o - C_{res}}{C_o} \cdot 100\%, \quad (4)$$

where, C_o is initial oil concentration in water, g / dm³;

C_{res} is residual oil concentration in water, g / dm³.

As can be seen from table 2 the purification degree of the water surface from oil at a contact time of more than 5 minutes is 98 – 99%. Obviously, the main part of oil is absorbed during the first five minutes, and desorption of oil from the material pores is not observed during 60 minutes.

Table 2. Time Dependence of Purification Degree of Water from Oil.

Time, min	Degree of Purification, %
1	93.5
5	98.7
15	98.9
30	98.9
45	98.8
60	98.9

The data in table 2 shows that the water purification from oil is not complete, therefore, the toxicity analysis of purified water by the biotest method was carried out. Crustaceans *Daphnia magna straus* were used as test objects. Analysis of contaminated water and water purified with mixed leaf litter samples showed decrease of the harmless substances concentration, which causes death of no more than 10% of test organisms with HCWD₁₀₋₄₈ = 717 in not purified water to HCWD₁₀₋₄₈ = 260 (HCWD is harmless concentration of water dilution) in water purified by the original sample of mixed leaf litter. The death of microorganisms in the aquatic environment during oil sorption by the original mixed litter decreases by more than 2.5 times.

Thus, the use of leaf litter to clean water surface from oil slicks is rational, as it has properties of adsorption materials. Therefore, it can be recommended as a bulk sorption material, a filler for booms, mats for collecting oil from water surface.

3.2 Variants of Technological Design of Oil Collection from Water Surface Using Mixed Leaf Litter.

There are many modern methods to collect oil from water surface [16]. One of the most used technological solutions is use of the examined samples as filler in mats (Figure 4) sized 10,250.05 m and weighing of 1 kg. Polymer net resistant to oil and with a mesh sized 66 mm in the transverse and longitudinal directions is selected as a shell. The dimensions and loading of the mat may vary depending on the area of contamination.

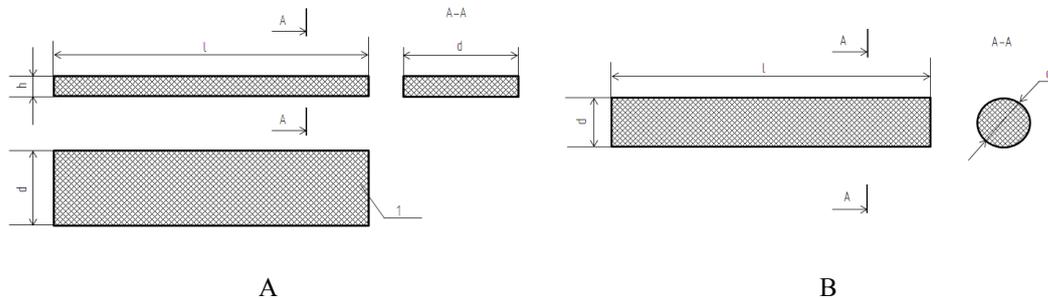


Figure 4. **A** – Absorbent mat ($l=1000-3000$ mm, $d= 250-2000$ mm, $h=50-400$ mm): 1 – polymer net; **B** – Sorption bolster ($l=1000-3000$ mm, $d= 120-500$ mm).

The use of mixed leaf litter samples as stuffing in mats was tested on a water body (untitled stream) in the area of company Kara Altyn Enterprise activity. The stream was blocked by two sorption mats set across the entire width of the water body. Sampling during the testing was carried out 1 m higher and lower the mats in the water. The oil content before passing through the sorption boom was 99.68 g / dm^3 , and after sorption - 0.09 g / dm^3 . Hence, the purification degree of the water surface from oil slick during industrial tests was 99%.

As the next technological solution for localization of oil slicks on the water surface, as well as preventing oil from entering the coastline, defence booms and shoreline shielding booms are used. Adsorption material based on the leaf litter is recommended for use in a universal design boom. The boom structure contains a bolster made of sorption material, shown in Figure 4 B, as well as a mat shown in Figure 4 A.

The sorption bolster is made similarly to the mat and can be used both as an independent sorbing agent and as part of a universal boom, the design of which is shown in Figure 5.

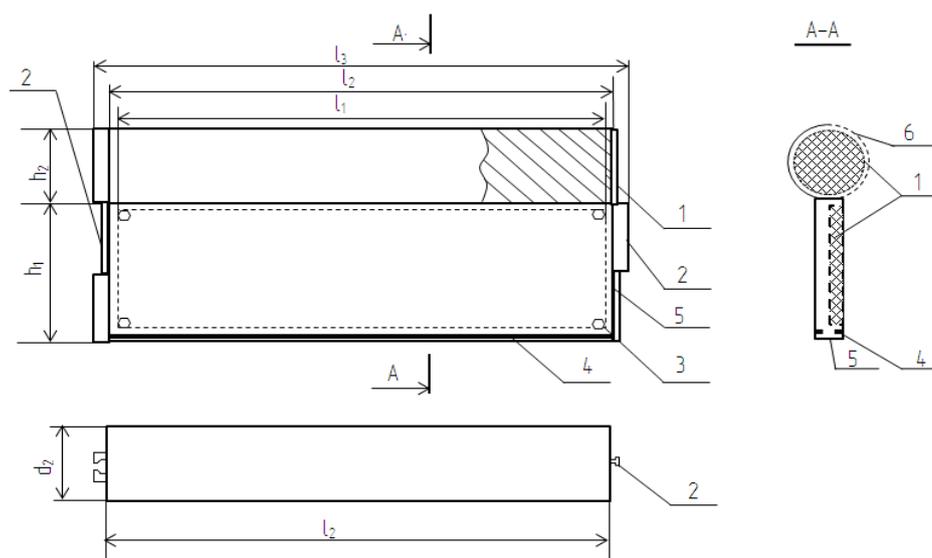


Figure 5. Universal sorbing boom 1 – sorbing element (leaf litter), 2 – bracing, 3 – bracing for a sorption mat, 4 – ballast, 5 – shell, 6 – polymer net.

The sorbing boom is made of polyvinyl chloride (PVC) shell 5, which is resistant to oil, radiation and microorganisms. The sorbing mat size can be selected depending on the water body and the nature of the oil slick. Iron or steel galvanized chains, cables, etc. can be used as a load 4 and for trawling. The booms are interconnected by bracing 2. The upper part of the boom, designed for a filler in the form of a bolster, is made of two materials: one side of the circle is made of PVC, which prevents the passage of oil, the second half is made of a large polymer net 6. In this type of design the ready made bolster with sorption material 1 is placed inside the structure, for its replacement and further reuse of boom. With large volumes of pollution and high oil slick thickness, as well as with strong winds and waves over 2-4 points, the sorbing boom can be equipped with a mat as an additional sorbing element. Bracing 3 allows to place the boom vertically, with a sufficient counterweight of the ballast. The presented design can be used both for localization and for parallel liquidation of an oil spill. The frame of the structure can be used repeatedly if sorbing elements are replaced. Used oil-saturated bolsters and mats must be regenerated or disposed of.

One of the main aspects of industrial ecology is the absence of secondary pollution during industrial technological processes, therefore it is necessary to develop a technology for the safe disposal or regeneration of used adsorption materials.

For this purposes, a possibility of extracting sorbed oil from the sorbent pores was examined by determining the retention capacity of mixed leaf litter, which was 2.713 g / g. This indicates a slight desorption of the pollutant and futility of its extraction and regeneration. High consumption and cost of regenerating materials make this procedure economically inefficient, in addition, there is an issue with disposal or regeneration of spent solvents, which leads to repeated environmental pollution. Thus, it is proposed to utilize the spent mixed leaf litter in oil sludge thermal processing plants for complete thermal decomposition of oil and leaf litter. After burning 1 kg of spent adsorption material 95 mg of ash is produced. In order to determine its hazard class, an elemental analysis was performed (table 3).

Table 3. Concentration of elements in the ash, in mass fractions over 100%.

Zn	Cu	Fe	Mn	Ni	Ti	V	Ca	K	Cl	S	P	Si
0.2	0.2	4.5	1.6	0.1	0.2	0.5	51	12	3.7	23	0.1	2

Thus, heavy metals are found in the ash in a low concentration, and elemental sulfur and calcium, which is the basis of the waste, are non-toxic and of low hazard. Thus, the ash from the burning of spent oil saturated leaf litter has a hazard class IV and can be disposed of at solid municipal waste landfills.

Conclusion

Studies have shown that mixed leaf litter, which is a waste from urban areas, can act as adsorption material. The sorption capacity of mixed leaf litter for oil is 8 - 10 g / g, which is higher than that of most adsorbents on plant and mineral basis. Visual observations show that oil does not stick to the leaf surface, but passes through into its pores, which indicates a high holding capacity of the material. The values of the contact angle indicate the hydrophobicity of the material and the selectivity to oil absorption. The purification degree of water surface from oil using mixed leaf litter was 98 - 99% and a decrease in water toxicity (2.5 times) confirms that the mixed leaf litter is an effective adsorption material. Use of the plant waste is possible both in bulk form and in the form of fillers for technological shells. The presented equipment options allow to choose methods for specific cases of spills, taking into account size of the oil slick and weather conditions. The ash values and the results of the analysis of ash after thermal combustion of oil-saturated waste show that the resulting waste is non-hazardous and is formed in small quantities. Thus, mixed leaf litter can be considered as an effective and technologically applicable adsorption material for the accidental oil spills response on water surface.

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