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Investigation of Sorption Properties of Wood Waste During Oil Spill Response

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Abstract: This work is devoted to the development and evaluation of an innovative sorbent for use in oil pollution, based on the modification of softwood sawdust. The research is aimed at creating an affordable, environmentally friendly and economically profitable material capable of effectively solving the problem of pollution of water bodies with oil and petroleum products. The process of modification of sawdust using a paraffin coating to achieve optimal sorption properties has been studied. The ability of the modified material to absorb petroleum products was analyzed, including the determination of its oil capacity and sorption rate. This development can make a significant contribution to solving environmental problems in regions with developed timber processing and oil production industries.

1 INTRODUCTION

The relevance of this study is due to the large-scale negative impact of petroleum products on aquatic ecosystems, especially in the context of the intensive development of the oil production and processing industry. Annual oil spills (from 2 to 10 million tons) lead to catastrophic consequences.: disruption of gas exchange and long-term pollution of water areas.

The problem is particularly important in regions with the use of water bodies for cargo transportation, such as the Yenisei River in the Krasnoyarsk Territory, which has been repeatedly polluted. Existing methods of oil spill response, including mechanical, chemical, and biological methods, often have low efficiency, high cost, or unjustified environmental risks (Zaitseva, Kulagina, Kulagina, 2024; Kulagina, Zaitseva, Kulagin, 2024). Sorption purification is one of the most effective methods. The use of available natural materials, such as sawdust, which is produced in fairly large volumes at woodworking enterprises, is an economically and environmentally promising proposal. Thus, the purpose of the study is to determine the possibility of using modified coniferous sawdust as a sorbent for cleaning water bodies from petroleum products and to develop recommendations for their use with subsequent thermal disposal.

The main mechanism of sorption of petroleum products by sawdust is physical adsorption and capillary impregnation. Petroleum products are retained in the porous structure of wood due to Van der Waals forces and surface tension. The key role is played by lignin and cellulose, which are the main components of wood. Due to them, the property of hydrophobicity is manifested, which contributes to the selective sorption of petroleum products above water. Sawdust has a well-developed system of macro- and micropores that act as capillaries, capturing and retaining petroleum products.

In the study (Veprikova, Tereshchenko, Chesnokov, Shchipko, Kuznetsov, 2010), a wood-polystyrene fibrous material for collecting oil and petroleum products was obtained, containing aspen bark as a filler (10-60 wt.% fraction 0.5-1.0 mm). The formation of fibrous composites occurred during the explosive hydrolysis of a mixture of expanded polystyrene and aspen bark under fairly mild conditions (process temperature 130 ° C, time 60 ° C, pressure 3 MPa) and without the use of binders. All the investigated wood sorbents demonstrate 100% buoyancy after oil collection for 24 hours.

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In (Pan, Gonoshilov, Kablov, 2010), the possibility of obtaining complex-type sorption materials based on various crushed plant raw materials (sawdust, cane) obtained by special heat treatment and subsequent modification was investigated. The pyrolysis process was used to obtain various sorbents from crushed vegetable raw materials. Pyrolysis of crushed reeds is carried out in a chamber equipped with outlet valves in the absence of oxygen. Depending on the conditions of the pyrolysis process, materials with different sorption characteristics were obtained. It has been established that the regime parameters of pyrolysis have a key effect on the formation of the porous structure and, as a result, on the sorption properties of the final products. The tests carried out revealed the selectivity of the materials obtained, while the reed sorbent showed maximum efficiency with respect to diesel fuel, while the sawdust–based sorbent showed maximum efficiency with respect to transformer oil. A synergistic effect is achieved with the combined use of sorbents, which resulted in the intensification of the sorption process of petroleum products and a reduction in the absorption time of petroleum products to 10-15 minutes.

2 METHODS

Within the framework of this study, a series of experiments was performed, including the preparation of sorption material, determination of the oil capacity of sawdust of various fractions; investigation of sorption properties; evaluation of the effectiveness of thermal utilization of spent sorbent (Galiullina, 2020).

2.1 Determination of oil capacity of sorbents

The oil capacity of sorbents is an indicator responsible for the amount of petroleum product absorbed by the sorbent per unit of its mass. The methods described in (Standard Test Method for sorbent performance of adsorbents (AM F726-99); TU 214-10942238-03-95) were used to determine oil capacity under static conditions.

The standardized ASTM F726 Methodology (current edition F726-17), designed for comparative analysis of the adsorption capacity and regenerability of granular or powdered adsorbents, allowing an objective comparison of the quality of adsorbents, control their production and assess suitability for applications requiring regeneration. In Russia, the method of determining oil capacity and moisture capacity is used (TU 214-10942238-03-95). The essence of the method is to simulate the sorption conditions of petroleum products when the sorbent is coated with a layer of test petroleum product and kept for 24 hours to achieve equilibrium saturation. This technique has been developed specifically to evaluate the effectiveness of sorbents used in the elimination of emergency oil and petroleum product spills in the water areas.

The experiment involved 3 samples: 1 – coniferous sawdust (finely dispersed, 0.5 mm fraction); 2 – coniferous sawdust (coarse, 2 mm fraction); 3 – coniferous sawdust 2 mm, treated with petroleum paraffin. Taking into account the studies conducted in (Filina, 2011), samples 1 and 2 were subjected to thermal activation (drying in a drying cabinet at 100 °C for an hour). In the first series of experiments, the test sorbent weighing 10 g was placed in a non-woven propylene bag (the oil capacity of the empty bag was preliminarily determined), shown in Fig. 1a, which was then placed in a glass and filled with petroleum products in Fig. 1b. After the expiration of time (10 minutes), the package was suspended from the lower hook of the RUNIS 6-140 scales, the values were fixed to a constant mass. The mass was considered constant, unchanged for 3 minutes.

a) b)

Figure 1: Conducting the experiment (a – prepared samples; b – immersion of the sample in petroleum product).

In the second series of experiments to determine the oil capacity, a sorbent weighing 10 g was placed on glass and oil product was added drop by drop for 3 seconds until it was completely absorbed (Fig. 2) The glass with oil product and sorbent was weighed.

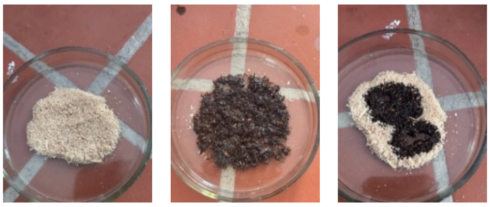

Figure 2: Conducting an experiment.

A visual experiment was performed to compare the data obtained. Modified sawdust (sample 1) and polymer sorbent "Unisorb" (sample 2) were taken as samples (Fig. 3).

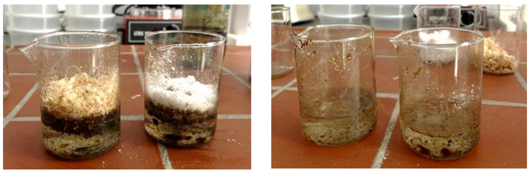

Figure 3: Sample 1 – Sawdust modified with paraffin; Sample 2 – Polymer sorbent "Unisorb".

For a comparative analysis of the rate of absorption of petroleum products by various sorption materials, an experiment was conducted under the following conditions:

1. Water contaminated with petroleum products was placed in two identical containers with the formation of a surface oil film of controlled thickness.
2. A natural sorbent (sawdust) modified with a paraffin coating was poured into the first vessel, and a synthetic polymer sorbent was added to the second. The materials were introduced simultaneously to ensure comparable conditions.
3. The time required for the complete removal of the oil film from the water surface by each of the studied sorbents was recorded.

2.2 Investigation of natural sorbent buoyancy

The buoyancy of a sorbent is its ability to stay on the surface of water, which is important for collecting petroleum products and other hydrophobic contaminants. The factors affecting the buoyancy of the sorbent are as follows: porosity and density – the lower the density and the larger the pores, the better the buoyancy; hydrophobicity – the ability to repel water and not absorb it; material structure – fractional composition (Kovalenko Shershneva, 2023).

When oil or oils are absorbed, buoyancy may decrease. Therefore, in the next series of experiments, softwood sawdust treated with paraffin was placed in a container with water contaminated with petroleum products to evaluate the effectiveness of sorption properties on the water surface. after the spent sorbent was collected from the surface of the water, the oil film was not visually observed, the recorded processing time (film absorption) was 4 minutes. The hydrophobicity of softwood sawdust modified with paraffin is shown in Fig. 4.

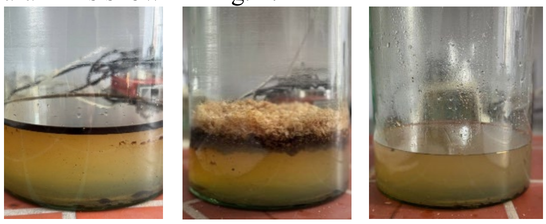

Figure 4: Water contaminated with petroleum products before and after the use of natural sorbent.

To assess the buoyancy of sawdust modified with paraffin, an experiment was conducted in which sawdust was placed in an aqueous medium containing an oil film in order to study their sorption capacity and resistance to immersion. After the sawdust surface was completely saturated with the oil phase, the sample remained under control for 48 hours. The evaluation criterion was the retention time of the sorbent on the water surface, taking into account the additional mass of the sorbed petroleum product.

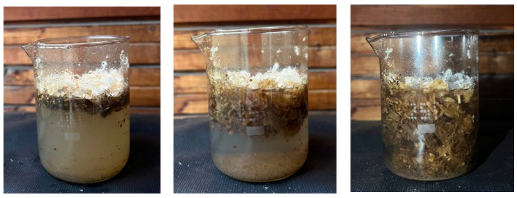

Figure 5: The proposed sorbent works at the beginning of the experiment, after 24 hours and 48 hours of exposure.

2.3 Conducting an experiment on a polluted section of the Yenisei River

To verify laboratory data on the sorption efficiency of modified sawdust in real conditions, an experiment was conducted in the water area of the Yenisei River in the city of Krasnoyarsk. Experimental work was carried out on a site with a visually fixed oil film showing a characteristic iridescent color.

Before application, sawdust was subjected to surface modification by paraffin hydrophobization and conditioning to a humidity of 12 ± 0.5%. Then the sorbent was evenly distributed over the surface of the polluted river area of 1 m2 with a dosage of 200 g/m2 (Fig. 6). The contact time with the oil film was 20 minutes under the following hydrological conditions: The current velocity is 1.2–2.0 m/s, the water temperature is 12 °C, the wind effect is 3 m/s.

Next, the sorbent was mechanically collected using specialized mesh devices (Fig. 7). The effectiveness of the process was assessed by the visual disappearance of the iridescent film and the degree of swelling of the sorbent.

Figure 6: The work of the sorbent on the Yenisei River.

Figure 7: The collected sorbent from Yenisei River.

2.3 Investigation of the possibility of utilization of spent natural sorbent by thermal method

Fuel pellets were obtained from a natural sorbent saturated with petroleum products in the laboratory using special granulator nozzles (Fig. 8).

Figure 8: Pellets obtained from oil-saturated sorbents

Pellets were examined for thermophysical properties. The flash and smoldering temperatures, as well as the ash content, were determined in laboratory conditions.

The flash point was determined in a laboratory furnace with automatic temperature control.

To determine the smoldering temperature, the sample was placed in a ceramic crucible and placed in the center of the same furnace. The heating was carried out in two stages: the first – up to 150 ° C at a rate of 10 °C per minute, the second - up to 250 °C at a rate of 5 °C per minute, with the temperature of the beginning of visual smoldering fixed until smoke without flame appeared. At the same time, mass losses were recorded, and the crucible was weighed several times before irreversible mass loss (>3% of dry weight) began (Fig. 9).

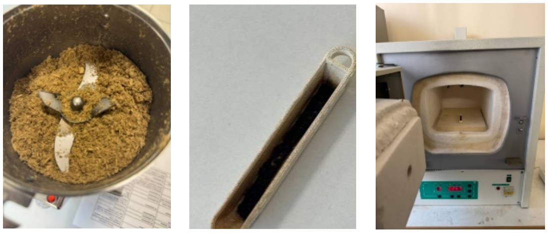

Figure 8: Conducting an experiment

3 RESULTS

The calculation of oil capacity was carried out according to the methods (Veprikova, Tereshchenko, Chesnokov, Shchipko, Kuznetsov, 2010; Pan, Gonoshilov, Kablov, 2010) using formulas 1 and 2. The calculated values are given in Table 1.

$$HE = \frac{m_1-(m_2+m_3)}{m_3}, \text{ g/g} \quad (1)$$

where m_1 – weight of the package with the sorbent attachment and the retained oil product, g; m_2 – weight of the package, taking into account the oil product retained, (blank sample), g; m_3 – the mass of the sorbent suspension. g.

$$HE = \frac{m_4}{m_5}, \text{ g/g} \quad (2)$$

where m_4 –mass of petroleum product absorbed by the sorbent, g; m_5– weight of the sorbent suspension, g.

Table 1: The results of experiments to determine the oil capacity of sorbents.

№	The value of oil capacity, g/g	
	ASTM F726	TU 214-10942238-03-95

1	1,641	1,620
2	2,454	2,412
3	2,571	2,514

A comparative analysis of the results of an experiment to determine the rate of absorption of petroleum products by sorbents showed that the polymer sorbent demonstrated complete absorption of petroleum products in 1.5 minutes, paraffin-modified sawdust ensured the removal of the oil film in 40 seconds, which indicates a higher sorption rate compared with the synthetic analog.

Analysis of the hydrophobic properties of sawdust treated with a paraffin coating demonstrated high hydrophobicity, which is confirmed by their stable buoyancy for 24 hours. The absence of immersion during this time indicates an effective modification of the surface that prevents wetting with water, as well as the preservation of a porous structure that provides sufficient buoyancy even after the sorption of petroleum products.

Smouldering is the slow, flameless burning of porous materials with limited oxygen access. Gorenje for wood pellets, this process begins when a critical temperature is reached, when the thermal decomposition of the components (mainly lignin and cellulose) leads to the release of volatile substances without an open flame (Oshkin, 2023). The results are shown in Table 2.

Table 2: Experimental values obtained.

Parameter	Meaning
Temperature of the beginning of smoldering, °C	170
Temperature of the active smoldering phase, °C	240
Critical mass loss, %	9
Flash point, °C	300

The ash content of pellets is the mass fraction of the nonflammable mineral residue after complete combustion of the sample at standard temperature. This indicator characterizes the uniformity of raw materials (absence of bark, sand, impurities), the corrosion activity of ash, as well as compliance with standards (EN ISO 17225, GOST 33103.1-2014).

After critical heating of the sample and fixation of a constant mass, the ash content of the obtained pellets was calculated according to formula 3 and amounted to 0.17%.

$$A_{ash\ level} = \frac{m_3 - m_2}{m_1} \cdot 100, \% \quad (3)$$

where m_1– weight of the dry sample, g; m_2– the mass of an empty crucible, g; m_3– масса тигля с золой, g.

Thus, the ash content of the obtained fuel pellets corresponds to pellets of the standard level according to EN ISO 17225-2.

4 CONCLUSIONS

Coniferous sawdust modified with a paraffin coating demonstrated a high sorption capacity in relation to petroleum products during the study. The maximum oil capacity was 2.57 g/g, which exceeds the performance of unmodified samples from the same material. The accelerated sorption kinetics of modified sawdust may be due to the increased wettability of petroleum products due to the paraffin coating and the optimal ratio of porosity and specific surface area of the material.

A comparative analysis of the absorption rate of petroleum products has shown that modified sawdust removes the oil film twice as fast as that of the synthetic polymer sorbent Unisorb. This indicates the high efficiency of the proposed natural sorbent.

In addition, the modified sorbent demonstrated a high buoyancy index. This is a key property and ensures their applicability for the elimination of emergency spills in the water areas and the possibility of subsequent mechanical collection.

An experiment in dynamic conditions conducted in the water area of the Yenisei River confirmed the effectiveness of modified sawdust in real conditions. The visual disappearance of the iridescent oil film in the controlled area after applying the sorbent proves its practical suitability for water treatment.

The spent sorbent saturated with petroleum products can be successfully processed into fuel pellets. A study of their thermophysical properties has shown that they are characterized by a low ash content corresponding to the EN ISO 17225-2 standard. The temperature of smoldering and flash points to the possibility of their safe use as an alternative solid fuel and the closure of the sorbent life cycle.

Softwood sawdust modified with paraffin is a highly effective, affordable and environmentally promising sorbent for the elimination of oil pollution of the water surface. The combination of high oil capacity, sorption rate, stable buoyancy and the possibility of subsequent thermal utilization into valuable energy raw materials makes this technology a comprehensive and economically feasible solution for use in regions with developed timber processing and oil production industries.

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