Removal of oils from water surfaces with modified Linden sawdust

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Abstract. The paper investigated the possibility of using modified woodworking waste to remove heavy oil products from the water surface by sorption. Sawdust of a heart-shaped linden tree (Tilia cordáta) was used as sorption materials and used diesel engine oil was used as a sorbate. In order to improve the sorption capacity and increase the sorption capacity of wood waste, they were treated with ultrasound at a frequency of 35000 Hz in an aqueous medium for 4 hours. The physical and mechanical characteristics of modified sawdust have been determined: bulk density, ash content, buoyancy. Experiments on modeling engine oil spills on the water surface have shown that linden sawdust, subjected to ultrasonic action, are effective sorption materials in relation to used diesel engine oil. The degree of water purification under static adsorption conditions reaches 99%.

1. Introduction
Purification of surface and wastewater from oil products is an urgent environmental and engineering problem in connection with the increasing volumes of production and consumption of various oil refined products. Pollution of reservoirs with oil products is largely due to the ingress of used engine, transmission, industrial oils, and cutting fluids into them. When entering the aquatic environment, hydrocarbons that make up petroleum products undergo various migration and transformation processes, of which the most important are dissolution, which is more characteristic of low molecular weight components, evaporation of light fractions, and sedimentation at the bottom of the reservoir. The prevalence of certain processes depends on the group and fractional composition of oil products and external conditions: temperature, pressure, humidity.

In contrast to oil, used motor oils contain products of oxidative polymerization and polycondensation of hydrocarbons, including resins, asphaltenates, polynaphthenic acids, carbenes and other types of compounds. Of particular danger are polycyclic aromatic hydrocarbons (PAHs), nitro-substituted PAHs, chlorinated biphenyls and their derivatives, formed as a result of chemical transformations of oil hydrocarbons during engine operation under the influence of high temperature, pressure, catalytic influence of various components of oils and additives.

Low biodegradability, high toxicity and cumulative properties of waste oils, significant volumes of their entry into the environment make the problem of cleaning aqueous media from them urgent.

To remove oil products from water bodies, mechanical, biological, physicochemical, and chemical methods are used; the most effective and environmentally friendly is the use of sorbents. For sorption treatment of waste and surface waters, along with industrial oil sorbents, organic cellulose-containing wastes from agriculture, woodworking and forestry are proposed [1-4]. At all stages of wood processing and processing, a large amount of waste is generated that is not used in production; often the volume of waste is greater than the volume of finished products.
The disadvantage of woodworking waste, which limits their widespread use for sorption water purification, is the lower sorption capacity compared to industrial sorbents. To improve the sorption capacity of cellulose-containing wastes, various methods of their modification are proposed: treatment with surfactants [5], solutions of inorganic and organic acids [6-8], alkalis [9], salts [10], organic compounds of various classes [11, 12]. The search and development of new methods for modifying sorption materials based on wood waste is an important and urgent task.

2. Materials and methods

In order to improve the sorption properties, the sawdust was treated with ultrasound at a frequency of 35000 Hz for 4 hours. For this, 10 g of sawdust was placed in flat-bottomed flasks with a volume of 250 cm$^3$, 100 cm$^3$ of distilled water was poured in and processed in an ultrasonic installation at a temperature of 25 °C. Then the sawdust was washed with distilled water to remove soluble compounds and dried to constant weight at 70 °C [13].

The ash content of the sawdust was determined by the gravimetric method. In a porcelain crucible, brought to constant weight at (600 ± 10) °C, 1–2 g of sawdust was placed, and after weighing, the crucible with the sample was calcined for 5 hours at the indicated temperature until the organic part of the sample was completely burned out and a constant weight was reached. After cooling in a desiccator, the crucible with the ash residue was weighed.

The ash content of the analytical sample A in percent by weight was calculated by the formula (1) taking into account the conversion factor for humidity:

$$A = \frac{m_3 - m_1}{m_2 - m_1} \cdot k \cdot 100$$  (1)

Where: $m_1$ – crucible weight, g; $m_2$ – crucible weight with sample, g; $m_3$ – weight of the crucible with ash, g; $k$ – moisture conversion factor.

The buoyancy of modified sawdust was determined by the method proposed by F A Kamenshchikov for oil sorbents. A sample of sorption material weighing 3 g was placed in a 50 ml beaker, half filled with water. The time of contact of sawdust with water was 72 hours. After the specified time, the sawdust remaining afloat was removed and dried at a temperature of 105 ± 1 °C to constant weight. The mass difference was used to determine the amount of drowned sorption material and buoyancy in percent [14].

To determine the bulk density, sawdust was poured in portions of 20 cm$^3$ into a cylinder with a volume of 100 cm$^3$. The cylinder was gently tapped with its bottom on a wooden disk for 1 minute in an inclined position, then weighed on an analytical balance.

Determination of the hygroscopic moisture content of modified linden sawdust was carried out by the gravimetric method. Weighed samples of the analyzed material in glass bottles were kept at a temperature of (105 ± 2) °C until constant weight. In this case, the first weighing was carried out no earlier than 10 hours after the start of drying.

The moisture content of the sample (W) in percent was calculated by the formula (2) with rounding not more than 0.1%

$$W = \frac{m_1 - m_2}{m_2 - m_0} \cdot 100$$  (2)

Where: $m_0$ – weight of the bottle, g; $m_1$ – weight of the weighing bottle with sample before drying, g; $m_2$ – weight of the sample bottle after drying, g.

The simulation of the removal of films of used oil from the water surface was carried out in laboratory conditions, for which a pre-weighed brass mesh was placed in a Petri dish, 50 cm$^3$ of distilled water was poured, then a certain amount of used engine oil (3, 5, 7 or 9 cm$^3$). An even layer of 1 g of sorption material was applied to the surface of the formed oil film. After 15 minutes, the sorbent was removed and weighed on an analytical balance to determine the total oil absorption and water absorption.
Then the mass of the oil product remaining in the Petri dish and the oil absorption of sawdust under the experimental conditions were determined separately. The method of determination is based on the extraction of waste oil from water with carbon tetrachloride, which, by dissolving the oil product, turns brown. The concentration of the dissolved engine oil was determined spectrophotometrically. The mass difference was used to determine the amount of absorbed oil, then - sorbed water [15].

The kinematic viscosity of the used engine oil was determined with a capillary viscometer, the density - by the pycnometric method.

3. Results and discussion

The removal of oil products from the water surface with modified wood waste was investigated.

Linden sawdust formed as waste at a woodworking enterprise of the Republic of Tatarstan was used as sorption materials. Since the original wastes were polydisperse in their particle size distribution, they were subjected to fractionation, and later, the most massive fraction with a particle size of 1–2 mm was used to modify and determine the physicomical and sorption properties. In order to increase the sorption capacity, wood waste was subjected to ultrasonic treatment for 4 hours, after which it was used in experiments to simulate the removal of oil films from the water surface.

An oil product with a high molecular weight and a heavy fractional composition - waste all-season diesel oil from a KAMAZ automobile - was studied as a sorbate. Some physicochemical characteristics of the sorbate are presented in table 1.

**Table 1. Physical and chemical characteristics of used motor oil.**

| Parameters                              | Value   |
|-----------------------------------------|---------|
| Density at 20 °C, kg/m³                 | 881.0   |
| Density in degrees API                  | 29.2    |
| Kinematic viscosity at 100 °C, mm²/s    | 10.5    |
| Kinematic viscosity at 40 °C, mm²/s     | 97.6    |

The efficiency of sorption water purification from oil products depends on their viscosity and density, since when using cellulose-containing sorption materials, not only sorption, but also adhesive interaction between the sorbent and the sorbate occurs. Used engine oil has increased values of kinematic viscosity at 100 °C and 40 °C and density at 20 °C, which is due to the presence of high molecular weight products of oil aging formed during engine operation under the influence of high temperature, atmospheric oxygen, catalytic effect of variable valence metals. The presence of oxidative polymerization products containing polar chemical bonds promotes an increase in the sorbate-sorbent interaction, an increase in adsorption, and an increase in adhesive bonds.

The possibilities of using cellulose-containing production wastes as sorption materials largely depend on their properties, such as bulk density, buoyancy, moisture content, and ash content. The main physical and mechanical characteristics of linden sawdust subjected to ultrasonic treatment for 4 hours in an aqueous medium are presented in table 2.

**Table 2. Physical and chemical characteristics of modified Linden sawdust.**

| Parameters                          | Value       |
|-------------------------------------|-------------|
| Packed density, g/cm³               | 0.106±0.004 |
| Buoyancy, %                         | 69.7±4.2    |
| Humidity, %                         | 3.57±0.05   |
| Ash content, %                      | 0.266±0.054 |

The modified sawdust has a fairly high buoyancy index (69.7%) and a relatively low bulk density (0.106%), which indicates a high porosity of the material and the presence of a highly developed interface.

The low ash content of modified linden sawdust (0.266%) indicates the possibility of their efficient utilization by incineration after the completion of the cleaning process with the formation of a small amount of non-combustible mineral waste.
The possibility of using ultrasonicated linden sawdust to remove films of used engine oil from the water surface was investigated. For this purpose, oil pollution was simulated in laboratory conditions: 3–9 cm³ of used engine oil was poured onto the surface of 50 ml water. The contact time of the sorption material and the sorbate was 15 minutes.

When entering water bodies, sawdust is capable of adsorbing, in addition to oil products, also water, therefore, along with oil absorption, water absorption was determined, as well as the total value of oil and water absorption. The efficiency of water purification was calculated as the ratio of the mass of the oil product sorbed by sawdust to its initial mass, which in different experiments was 2.643 g, 4.405 g, 6.167 g, 7.929 g. The results are presented in Table 3.

The degree of purification in all considered examples exceeds 99%, which indicates a high sorption capacity of the ultrasonically modified linden sawdust.

It should be noted a significant decrease in water absorption with an increase in the thickness of the oil film: with an increase in the volume of oil in water by a factor of 3 from 3 cm³ to 9 cm³, water absorption decreases from 1.013 to 0.361 g of water per 1 g of sorbent. In general, the low value of water absorption indicates a significant hydrophobicity of the modified sorption material, which, apparently, is the result of ultrasonic treatment.

### Table 3. Results of modeling the removal of motor oil from the water surface with modified Linden sawdust.

| Volume/weight of motor oil, cm³/g | Total motor oil sorption capacity and water uptake, g/g | Water uptake, g/g | Motor oil sorption capacity, g/g | Motor oil removal efficiency, % |
|----------------------------------|--------------------------------------------------------|-------------------|---------------------------------|--------------------------------|
| 3/2.643                          | 3.654                                                  | 1.013             | 2.641                           | 99.95                          |
| 5/4.405                          | 4.400                                                  | 0.812             | 5.212                           | 99.89                          |
| 7/6.167                          | 6.144                                                  | 0.551             | 6.695                           | 99.63                          |
| 9/7.929                          | 8.235                                                  | 0.361             | 7.874                           | 99.31                          |

As you know, ultrasound changes the morphological parameters of wood, while the destruction of macromolecular chains is accelerated and the processes of extraction in an aqueous medium of various substances are intensified: lignin, tannins, phenol derivatives [16, 17]. The consequence of ultrasonic action is a low bulk density and high buoyancy of the sorption material, indicating the presence of a highly developed porous structure, as well as high sorption activity with respect to non-polar sorbates.

The use of ultrasound as a method of physical modification of wood waste is safer and more environmentally friendly compared to chemical activation, which involves the use of solutions of mineral and organic acids, alkalis and other aggressive compounds and the formation of contaminated wastewater in the production of sorbents.

### 4. Conclusions

The high buoyancy (69.7%) and low bulk density (0.106%) of the sonicated linden sawdust indicate the presence of a highly developed interface. The results of experiments on modeling engine oil spills on the water surface showed that modified linden sawdust are effective oil sorbents, the degree of engine oil removal is more than 99%.

High buoyancy and high cleaning efficiency make it possible to use ultrasonically modified linden sawdust as a sorption load in booms when cleaning surface water from oil products.

The processing of sawdust and the production of sorption materials on their basis will reduce the volume of formation and accumulation of waste from the woodworking industry and reduce the area of alienated land for their placement. The resulting sorption materials provide effective removal of heavy oil products from the water surface and can be considered as an alternative to industrial sorbents.

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