Investigation of the Sorbing Properties of the Dahurian Larch Bark in its Interaction with Petroleum Products

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Abstract. As is known, pollution of the environment by oil products leads to the gravest consequences, the elimination of which is expensive for mankind. Thereby intensive researches of effective methods of liquidation of oil pollution are conducted now. Sorbents on a plant basis favorably differ by their ecological compatibility, availability and cheap material. In the present work, the problems of the development of a sorbent on the basis of modification of the bark of Dahurian larch, which grows mainly in Eastern Siberia and the Far East, in particular in the Republic of Sakha (Yakutia) are considered. The results of experimental measurements of the sorption capacity of the modified bark of the Daurian larch are presented.

1. Methods of obtaining a sorbent from the bark of larch

At present, petroleum products are one of the 10 largest polluters of the environment. Annual volumes of oil pollution in Russia are estimated at 10-12 million tons and in European countries 1.6 million tons per year [1]. According to the authors of [1] of all the above methods, at present, 20% of oil pollution is removed by the most inefficient and labor-consuming method - mechanical, 20% - with the use of modern sorbing substances, and 60% are not eliminated at all. It should be noted that in the scientific and practical literature of recent years there has been a steady interest in sorbents of plant origin [2-10]. One of the promising materials of plant origin, in Russia, is the tree bark, since Russia accounts for 21% of the world's timber reserves.

As a review of scientific, practical literature and Internet resources has shown, at present, several groups of researchers have formed in Russia on the intensive development of sorbents obtained on the basis of larch bark processing. Table 1 shows the main works, provides information on the methods of production of sorbents based on the bark of larch and their application.

Note that sorbents based on the larch bark, as a rule, are a by-product or residue from various processing of the bark in order to obtain various useful substances (extraction). As the results of [2] have shown, the sorption capacity of sorbents made of larch bark is quite high. In particular, for the activated bark of larch, the absorptive capacity with respect to the engine oil can reach 6.8 g/g, which indicates the prospects of research aimed at the development of sorbents of this type.
Table 1. Methods for producing sorbents on the basis of the bark of the larch and their application.

| №  | Researchers | Method | Application |
|----|-------------|--------|-------------|
| 1  | Rudkovsky AV, Fetisova O Yu., Chesnokov N V [2]. Kuznetsov B N, Golovina Yu G., Golovin V V, Eremina AO, Levdansky VA [3] | Pyrolysis, activation of larch bark previously extracted with various solvents | oil spills, fuel spills |
| 2  | Simkin Yu Ya., Besedina I N, Epifantseva [4,5]. Besedina I N, Ugay M Yu, Petrov V S [6] | Pyrolysis, activation of larch bark, briquetting | in chemical production in particular, butadiene production, wastewater treatment of chemical plants |
| 3  | Semenovich AV [7,8] | Chemical modification of larch bark after preliminary extraction | wastewater treatment from pollutants of various nature, liquidation of oil spills |
| 4  | Babkin V A, Ostroukhova L A, Malkov Yu A, Ivanova S Z, Ivanova N V, Medvedeva E N, Trofimova N N [9]. | Extraction processing of larch bark | cleaning industrial sewage and objects contaminated with oil products and phenols |

2. A method for increasing sorption properties

In this paper, the modified bark of Daurian larch growing mainly in Eastern Siberia and the Far East, in particular in the Republic of Sakha (Yakutia), is considered as a sorbent. One way to increase the sorption properties of the larch bark is to increase its porosity and hydrophobicity. We propose a simple method of increasing the porosity and hydrophobicity of the bark of Dahurian larch, based on its hydrothermal treatment in pure, salt-free water. Note that the resulting bark extract is used to make a natural dye.

The entire technological chain of manufacturing of sorbent from the larch bark consists of the following stages:

• Sifting of raw materials for cleaning from the bast and dead cells of periderm. The latter is due to the fact that sorbing properties are mostly due only to the periderm of the bark, and not the entire bark.

• Crushing of the bark by a rotor crusher to medium fractions 1-2 cm (length, width) and small 0.5 cm.

• Repeated sieving, in order to cleanse of poor-quality samples, and also sorting into fractions.

• Hydrothermal treatment of the crushed bark in the water cleared of salts and minerals by means of digestion in the KEEM-250 OM boiler with a mixer. Technical characteristics of the boiler: voltage 400 V, power 30 kW, type of current 3-phase with neutral, variable 50 Hz; quantity, nominal volume 250 liters, working steam pressure in steam-water jacket 100 kPa (1.0 kgf / cm2), water pressure in the water system from 49 to 589 kPa (from 0.5 to 6 kgf / cm2), water heating time up to 95 ° C for 80 minutes. The digestion was carried out at a temperature of 90 ° C-95 ° C, for 1.5 hours. As a result of digestion, an extract is retrieved, which was used as raw material for the production of natural dye. Residual product - the boiled larch bark was dried and subjected to sifting.

In order to determine the density treated with the above method of larch bark, the density of the starting material was measured before and after treatment. In this experiment, the density of the bark was determined on the basis of a measurement of the volume of the liquid containing samples of the larch bark by the following formula:
\[ \rho = \frac{m}{V_2 - V_1} \]  

(1)

where \( m \) is the mass of the sample of the larch bark, \( V_2 \) is the volume of the liquid containing the sample of the larch bark drowned by the piston, \( V_1 \) is the volume of the liquid without a sample of the bark.

### Table 2. Measurement results.

| №  | Bark           | Duration of stay in water, min | Density g/ml |
|----|----------------|-------------------------------|--------------|
| 1  | Crushed        | 0                             | 0.37         |
| 2  | Crushed and boiled | 0                             | 0.21         |
| 3  | Crushed        | 90                            | 0.57         |
| 4  | Crushed and boiled | 90                            | 0.38         |

The results of the measurements are shown in Table 2, where the averaged values of masses, volumes and densities determined experimentally for the four types of material studied are given. As can be seen from the table, the digestion of the larch bark reduced its density from 0.37 g / ml to 0.21 g / ml, i.e. on 42.5%. When we first impregnated the samples with water for 90 min, the difference in the densities of water-impregnated samples of treated (0.57 g / ml) and untreated (0.38%) bark was reduced to 34%. At the same time, due to impregnation with water, the values of the densities of the samples, both untreated and processed, increased due to their absorption of liquid. Thus, the density of the unboiled bark increased from 0.37 g / ml to 0.57 g / ml, i.e. on 54%. Similar figures for the cooked samples: 0.21 g / ml and 0.38 g / ml. an increase of 81%. Further, to determine the hydrophobic properties of 20 pieces of both digested and boiled bark were placed in a vessel with water and left in this state for 1 day. For the time being, none of the samples were immersed completely in the water.

Thus, when digested, the bark of larch becomes less dense. The decrease in the density of the cortex is due to the appearance of additional pores in the material during digestion (extraction).

### 3. Investigation of the sorbing properties of the larch bark

In this section, we consider the results of an experimental study of the sorption capacity of the larch bark, in two of its states: in untreated and processed. The purpose of the experiment was to determine the sorption capacity of untreated and processed larch bark during their interaction with petroleum products. The sequence of the experiment is as follows:

• A sorbent material weighing approximately 7-10 g is placed in a glass vessel with a previously measured mass \( m_0 \), and the total weight of the vessel \( m_1 \) and the sorbing material is measured prior to its interaction with the raw oil;

• The sorbate is poured into the glass vessel, the lid of the vessel closes and the timer switches on;

• After the set time period, the timer stops. The sorbate is poured out of the vessel through a sieve and the mass of the vessel with the sorbing material \( m_2 \) is measured;

• Sorption capacity is defined as the ratio of the mass of the oil product absorbed by the sorbent and the mass of the sorbent multiplied by 100% [2]:

\[
C = \frac{m_2 - m_1}{m_1 - m_0} \times 100\%
\]

(2)

In order to study the dynamics of sorption capacity in time, the measurements were carried out for various time intervals of the sorbent and sorbate interaction of 15, 30, 45, 60 min. As sorbates were selected: motor oil M-63/12G1, diesel fuel (summer), gasoline AI-92 and raw oil. Table 3 shows the experimentally determined sorption capacity of untreated bark.
Table 3. Sorption ability (C, %) of larch bark.

| Sorbate                  | Duration of interaction of untreated bark with sorbate, min |
|--------------------------|------------------------------------------------------------|
|                          | 15   | 30   | 45   | 60   |
| Gasoline Al-92           | 15.3 | 18.9 | 39.7 | 43.6 |
| Diesel fuel (summer)     | 30.4 | 37.7 | 129.4| 142.1|
| Engine oil M-63/12G1     | 35.7 | 57.2 | 234.3| 251.7|
| Raw oil                  | 32.6 | 32.6 | 79.5 | 83.5 |

As can be seen from the table, the unrestricted bark exhibits the highest sorption ability reaching to 251.7% with respect to motor oil with a reaction time of 60 min. The next sorbate of the well-absorbed unmodified bark is diesel oil 142%, also with an interaction time of 60 min. Next comes raw oil of 83.3% and in the very turn the worst is absorbed gasoline 43.5%. Note that the data on gasoline may not be accurate due to its extreme volatility. Since it could evaporate at the time of weighing the sample or pouring gasoline, thereby distorting the measured values.

Let us pass to the second kind of sorbent - ground and modified hydrothermal processing of the larch bark. Sorption capacity of this sorbent in relation to the sorbates under consideration for different duration of their interaction is presented in Table 4.

Table 4. Sorption ability (C, %) of modified larch bark.

| Sorbate                  | Duration of interaction between the treated bark and sorbate, min |
|--------------------------|------------------------------------------------------------------|
|                          | 15     | 30     | 45     | 60     |
| Gasoline Al-92           | 20.3   | 38.7   | 53.6   | 55.2   |
| Diesel fuel (summer)     | 41.6   | 65.8   | 148.3  | 163.7  |
| Engine oil M-63/12G1     | 67.7   | 97.4   | 323.2  | 352    |
| Raw oil                  | 38.8   | 54.3   | 166.4  | 175.5  |

Comparison of this table with the previous one (see Table 3) shows a significant difference in the sorption capacity of the modified bark as compared to the unmodified one. Thus, the sorption ability with respect to motor oil in Table 3 with an interaction time of 60 minutes equaled 251.7%, the corresponding value in the last table is approximately 352% or 1.4 times greater. In relation to gasoline, the increase is 1.27 times and 1.15 times for diesel fuel. A somewhat unexpected result was obtained for raw oil - 2.1 times and is 175.5%. For unmodified cortices, the sorption capacity with respect to raw oil was significantly inferior to that of diesel fuel. For the modified bark the situation changed 2 place after the engine oil sorption is occupied by raw oil, followed by diesel fuel and gasoline.

4. Conclusion
Experimental studies of the sorption capacity of two types of larch bark sorbents - unmodified and modified, in relation to raw oil, engine oil M-63/12G1, diesel fuel (summer) and gasoline Al-92 showed the following:

• Modification of the bark of Dahurian larch by digestion in purified water, leads to a significant increase in its sorption capacity in comparison with its natural state. The highest values for the sorption capacity of the modified bark demonstrate with respect to motor oil (352%). This ability is somewhat lower in relation to raw oil, diesel fuel and insignificant in relation to gasoline;
The sharpest increase in the sorption capacity of the modified larch bark is observed 30-45 minutes after the beginning of interaction with the sorbate, stabilizing (saturating) in the region of 60 minutes;

The values of the sorption capacity of the modified bark of larch in relation to oil and oil products determined according to the results of the experiment are close to those of other sorbents, including those used in the liquidation of oil spills, which indicates the possibility of using this type of sorbent in practice.

5. References
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