Features of Interaction of Crushed Daurian Larch Bark with Petroleum Products

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Abstract. The work summarizes a series of publications devoted to the study of the sorption capacity of the bark of the Daurian larch, in terms of studying the possibility of its use as a source material for the production of a sorbent for cleaning reservoirs from oil pollution. A simple method of processing the bark of Daurian larch is proposed, which leads to a significant increase in its sorption qualities. The results of experimental studies of the density and sorption capacity of larch bark, as well as the results of spectral studies of its structure, are presented. The conducted research allowed us to determine the mechanism of increasing the porosity of the bark of the Daurian larch during its hydrothermal treatment and, as a result, leading to a significant increase in sorption capacity.

1. Introduction
As you know, one of the most common environmental pollutants is oil and petroleum products. Every year in Russia, 10-12 million tons of petroleum products are poured into the surrounding area, the corresponding figure for European countries is 1.6 million tons [1]. Oil product pollution is particularly sensitive in the Northern regions of Russia, where the period of environmental recovery after pollution is much longer than in temperate regions. It is well known what consequences were caused by the diesel fuel spill in Norilsk in 2020 or the oil spill at the Talakan oil field in 2018. Note that in many localities in the North of Russia, electricity is still provided by diesel power plants. Recently, much attention has been paid in the scientific literature to materials of natural origin as raw materials for the production of sorbents. In particular, methods for obtaining sorbents from larch bark were studied in [2-7], where methods of pyrolysis and activation, chemical treatment, etc. were considered. In our opinion, the methods discussed in [2-7] are energy-intensive and technologically complex, so they lead to an increase in the cost of the final product. We have studied a simple and less energy-intensive method of processing larch bark, which significantly increases its sorption capacity.

2. Spectroscopy of larch bark after absorption of base oil and oil products
We selected the bark of the Daurian larch, which is the most common type of forest vegetation in the North-East of Russia, as the source material for making the sorbent. Earlier in [8], we studied the sorption capacity of Daurian larch bark crushed to a fraction of 0.5-1.5 cm.

Sorption capacity is defined as the ratio of the mass absorbed by a sorbent sorbate to sorbent mass, multiplied by 100%:
\[ C = \left( \frac{M_2}{M_1} \right) 100 \% \quad (1) \]

Where, \( M_1 \) is the mass of the sorbent and \( M_2 \) is the mass of adsorbed sorbate.

We consider a simple hydrothermal method (boiling) of processing the bark in water purified from salts and minerals at a temperature of 900°C-950°C and lasting up to 1.5 hours. Note that the crushed but not processed bark itself also has a sorption capacity. Comparison of the sorption capacity of crushed larch bark before and after its hydrothermal treatment showed that boiling the bark leads to a significant increase in its sorption capacity. For example, the increase in the sorption capacity of the treated crust relative to base oil was 210%. To study the internal structure of the crust, a spectral study was performed using the nanolaboratory "NT-MDT Integra" (JSC "NT-MDT", Zelenograd), the results of which are shown in Table 1.

**Table 1.** The values of the maxima of the Raman displacement cm\(^{-1}\) untreated bark of larch [8].

| Sorbate       | The larch bark separately | The sorbate separately | Sample of the sorbent after contact with the sorbates |
|---------------|---------------------------|------------------------|-----------------------------------------------------|
| Base oil      | A(1650)                   | A(432)                 | A(562)                                              |
|               | B(2038)                   | B(1313)                | B(1474)                                             |
|               | C(2360)                   | C(1764)                | C(1963)                                             |
|               | D(2733)                   | D(2321)                | D(2282)                                             |
|               | E(4074)                   | E(2674)                | E(2690)                                             |
|               | F(4400)                   | F(3981)                | F(4088)                                             |
|               | G(4609)                   | G(4379)                | G(4404)                                             |
|               |                           | H(4634)                | H(4609)                                             |
| Engine oil M- | A(1650)                   | A(494)                 | A(677)                                              |
| 63/12G1       | B(2038)                   | B(1424)                | B(1443)                                             |
|               | C(2360)                   | C(1963)                | C(1969)                                             |
|               | D(2733)                   | D(2288)                | D(2293)                                             |
|               | E(4074)                   | E(2664)                | E(2701)                                             |
|               | F(4400)                   | F(4379)                | F(4383)                                             |
|               | G(4609)                   | G(4580)                | G(4601)                                             |
| Diesel fuel   | A(1650)                   | A(307)                 | A(1474)                                             |
|               | B(2038)                   | B(1400)                | B(1957)                                             |
|               | C(2360)                   | C(1952)                | C(2349)                                             |
|               | D(2733)                   | D(2215)                | D(2701)                                             |
|               | E(4074)                   | E(2680)                | E(4012)                                             |
|               | F(4400)                   | F(3999)                | F(4400)                                             |
|               | G(4609)                   | G(4605)                |                                                      |
| Gasoline AI-92| A(1650)                   | A(744)                 | A(1644)                                             |
|               | B(2038)                   | B(1381)                | B(1986)                                             |
|               | C(2360)                   | C(1963)                | C(2332)                                             |
|               | D(2733)                   | D(2243)                | D(2754)                                             |
|               | E(4074)                   | E(2706)                | E(4396)                                             |
|               | F(4400)                   | F(4601)                |                                                      |
|               | G(4609)                   |                                                      |                                                      |

Base oil, diesel fuel, M-63/12G1 engine oil, and AI-92 gasoline were selected as sorbates. Table 1 shows the spectral maxima of separately sorbates, separately crushed bark, separately boiled bark bark.
(sorbent) and sorbent after interaction with sorbates. As can be seen from the table, in the range of wave numbers 4000-4500 cm\(^{-1}\), a number of clear lines are observed in the treated crust (sorbent), while such clear maxima are absent for the untreated crust [8]. Also, the sorbent does not have a peak in the region of E (3474), which is probably due to the evaporation of resins as a result of boiling. At the same time, the sorbent had two new peaks F(4400) and G(4609), which were absent in the untreated crust. In our next work [9], we studied the change in the density of crushed larch bark when it was boiled. Table 2 shows the densities of untreated and treated bark samples before and after immersion in water for 90 minutes.

### Table 2. Density measurement.

| Bark                  | Duration of stay in water, min | Density, g/ml |
|-----------------------|--------------------------------|---------------|
| Crushed               | 0                              | 0.37          |
| Crushed               | 90                             | 0.57          |
| Crushed and boiled    | 0                              | 0.21          |
| Crushed and boiled    | 90                             | 0.38          |

Wetting the samples in water leads to an increase in density, which is caused by water soaking into the porous structure of the samples. As, can be seen from the table, wetting the treated larch bark in water leads to an increase in the sample density from 0.21 g/ml to 0.38 g/ml, i.e. by 81%. Similar indicators for untreated bark are 37 g/ml, 0.57 g/ml, i.e. by 54%. Thus, the porosity of treated samples of larch bark increased by 2 times compared to samples of untreated bark.

Studies of the time dynamics of the sorption capacity of samples of sorbents made from the bark of Daurian larch and treated by hydrothermal method are presented in Table 3. As can be seen from the table, the maximum sorption capacity is observed approximately one hour after interaction with various sorbates and is 55.2% for AI-92 gasoline, 163.4% for diesel fuel, 175.5% for base oil and 352% for M-63/12G1 engine oil.

### Table 3. Sorption capacity (C %) of the sorbent sample.

| Sorbate                | Duration of interaction between the treated bark and sorbate, min |
|------------------------|---------------------------------------------------------------|
|                        | 15    | 30    | 45    | 60    |
| Gasoline AI-92         | 20.3  | 38.7  | 53.6  | 55.2  |
| Diesel fuel            | 41.6  | 65.8  | 148.3 | 163.4 |
| Engine oil M-63/12G1   | 67.7  | 97.4  | 323.2 | 352   |
| Base oil               | 38.8  | 54.3  | 166.4 | 175.5 |

### 3. Conclusion
The presented studies have shown that the bark of the Daurian larch, crushed to fractions of 0.5-1.5 cm, has a sorption capacity. Simple hydrothermal treatment of crushed bark samples in water at a temperature of 900°C-950°C and lasting up to 1.5 hours leads to a significant decrease in the density and, accordingly, an increase in the porosity of the samples, as evidenced by the study of the sample.
density. The reason for the increased porosity of samples of treated larch bark is probably the intensive
evaporation of resins contained in the bark, which evaporate mechanically expand the porous structure
of the samples. This mechanism is supported by the results of a spectral study of the treated cortex.
Thus, it was found that after hydrothermal treatment, the maximum E(3474) disappears in larch bark
(see table 1). In turn, an increase in the porosity of the samples leads to an increase in the sorption
capacity of the sorbent made from the treated bark of the Daurian larch.
Thus, the bark of the Daurian larch after hydrothermal treatment can be used as a sorbent for
cleaning the environment, mainly reservoirs from oil pollution. As can be seen from table 3, the
sorption capacity of this sorbent is quite comparable with the corresponding characteristic of other
known sorbents.
In the future, we plan to study the sorption qualities of the Daurian larch bark under conditions of
negative and extremely low temperatures typical for the North-East of Russia.

4. References
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