Obtaining Sorption Material from the Leaves of Aésculus Hippocastanum L.

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Abstract – Using waste of different genesis as sorption materials allows solving several problems at once such as decontamination of waste and reduction of production costs. The physicochemical properties of the products of thermal modification of Aésculus hippocastanum L. leaves, which are promising raw materials for the sorption material, were studied. It is established that the optimal modification temperature is 250 ºC. At higher temperatures, cellulose and levoglucosane are decomposed with a decrease in the total percentage of carbon from 62 to 10 mass.%. High purification efficiency of model emulsions containing industrial oil (91 and 97%) is achieved even at heat treatment temperatures of 150 and 250 ºC, respectively. With further increase in temperature the cleaning efficiency practically does not increase, therefore, a further increase in firing temperature is not rational.

Keywords – sorbent; water purification; waste processing; petroleum products; plant waste.

I. INTRODUCTION

The use of wastes of various genesis as sorption materials is becoming an increasingly popular area of scientific research and industrial development since it allows solving several problems at once such as waste disposal and reduction of production costs [1]. The sorption materials obtained by modifying such common wastes as saturation precipitation of sugar production from sugar beets, iron sand formed during the processing of household and industrial wastes, solid wastes from mining, such as gold, iron ore and polynematic ore, containing silicates and others are commonly known [2-6].

Plant waste often has a complex of physicochemical properties, due to which they can be used as sorbents in wastewater treatment from various pollutants. Their sorption capacity can be significantly increased by various modifications such as temperature, reagent, plasma exposure, etc. The affinity for certain pollutants, which served as the basis for many scientific studies, increased [7-13].

Despite the apparent similarity, cellulose-containing materials have differences in sorption capacity, pore volume, efficiency of extraction of various substances from aqueous media, therefore, research on the features and methods of modification and preparation of plant waste for use in water purification does not lose its relevance [13].

Deciduous waste of urban utilities is a widely available and virtually unclaimed material, especially in Eastern Europe. It is brought to landfills of household waste, and in view of large volumes of plant garbage this leads to an accelerated filling of the landfill capacity.

Since at present, for the sustainable development of the human community, a widespread and comprehensive reduction of the man-made load on natural systems is required, the search for ways to use such valuable material as tree waste is an urgent task.

The main pollutants of the hydrosphere include oil, petroleum products and their derivatives (phenols, organic acids, synthetic surfactants and other chemicals) [13-17]. Petroleum hydrocarbons (Table 1) belong to the category of
biologically persistent, hardly oxidizable organic pollutants and they are practically a danger due to the complexity of their purification, which is connected with a large variety of chemical compounds having the concept of “petroleum products” on the one hand and on the other hand with the presence of associated pollutants in the drainages [13-19].

<table>
<thead>
<tr>
<th>Components</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic or paraffin (alkanes)</td>
<td>15-55</td>
</tr>
<tr>
<td>Cycloparaffin (cycloalkanes, naphthenes)</td>
<td>30-50</td>
</tr>
<tr>
<td>Aromatic (gasoline and polynuclear compounds)</td>
<td>5-20</td>
</tr>
<tr>
<td>Asphalt compounds (asphaltenes, heterocyclic substances)</td>
<td>2-15</td>
</tr>
</tbody>
</table>

The difficulty of preventing the petroleum products dumping with wastewater is associated, on the one hand, with a large variety of chemical compounds falling under the concept of “petroleum products”, and on the other hand – with the presence of associated pollutants in wastewaters [20, 21].

For purification of wastewater from petroleum products and suspended solids a wide range of methods is used, in particular, adsorption methods [18, 19].

II. MATERIALS AND METHODS

Source resource – tree waste – was collected in the urban area of Belgorod (Russian Federation). Horse chestnut (Aesculus hippocastanum L.) is a common planting of city streets in many European countries. It is a tree with a thick crown, which leads to the formation of a large hardwood mass [22, 23].

The thermal treatment of the samples has been carried out in the muffle furnace LOIP LF-7/13.

Thermal Analysis (DTA) was carried out using derivatograph 431Q-1500 and equipment for synchronous thermal analysis STA 449 F1.

The analysis of peculiarities of the chemical composition and structure of CCP samples was carried out using the scanning electron microscope of high resolution TESCAN MIRA 3 LMU.

The specific surface area was measured via low-temperature nitrogen adsorption, the Sorbi-MS instrument.

Industrial oil I-20A was used as a sample of oil products. Purification of aqueous media from petroleum oil was carried out as follows: 100 ml of the emulsion was placed in a conical flask, and then a sample of sorption material was added and mixed by electronic stirrer for 20 minutes. After that the contents of the flask were left for sedimentation for 15 minutes. Clarified water was examined for petroleum oil concentration using concentratometer KN-3 (Russia).

The purification efficiency (E) was calculated according to the formula:

\[ E = \left( \frac{C1 - C2}{C1} \right) \times 100\% \]

where C1 and C2 – concentrations of substances before and after water purification, respectively.

III. RESULTS AND DISCUSSION

The following requirements are imposed on the sorption materials used to extract oil products from aqueous media: high sorption capacity, hydrophobicity, and economic rationality.

In accordance with the data given above, the following physicochemical characteristics of Aesculus hippocastanum L. (LAHL) leaves were studied: moisture, pH of the aqueous extract, bulk density, hydrophobicity, ash, specific surface area, and the content of the main chemical components of the leaves: cellulose, lignin, tannins.

The LAHL_initial sample and LAHL samples heat-treated at temperatures of 150-450 °C were examined. Table 2 shows the results of the study of physicochemical properties of LAHL.

<table>
<thead>
<tr>
<th>Determined parameter</th>
<th>LAHL_initial</th>
<th>LAHL_250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density (kg/m³)</td>
<td>30</td>
<td>42</td>
</tr>
<tr>
<td>Initial density (kg/m³)</td>
<td>1320</td>
<td>1510</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>4.80</td>
<td>4.60</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>1.2</td>
<td>1</td>
</tr>
<tr>
<td>pH of the aqueous extract</td>
<td>6.0</td>
<td>6.2</td>
</tr>
</tbody>
</table>

The values of the measured specific surface (Ss) are presented in Table 3.

<table>
<thead>
<tr>
<th>Treatment temperature (°C)</th>
<th>Sample mass (g)</th>
<th>Moisture (%)</th>
<th>Constant BET</th>
<th>Correlation Coefficient</th>
<th>Specific surface Sud (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.385</td>
<td>4.80</td>
<td>2</td>
<td>0.297</td>
<td>2.6 ± 1.6</td>
</tr>
<tr>
<td>150</td>
<td>0.385</td>
<td>2.50</td>
<td>19</td>
<td>0.9857</td>
<td>4.0 ± 0.4</td>
</tr>
<tr>
<td>250</td>
<td>0.454</td>
<td>3.00</td>
<td>48</td>
<td>0.9979</td>
<td>17.6 ± 0.6</td>
</tr>
<tr>
<td>350</td>
<td>0.395</td>
<td>2.70</td>
<td>88</td>
<td>0.9991</td>
<td>24.8 ± 0.6</td>
</tr>
<tr>
<td>450</td>
<td>0.434</td>
<td>2.40</td>
<td>46</td>
<td>0.9998</td>
<td>27.9 ± 0.4</td>
</tr>
</tbody>
</table>

As it can be seen from the results presented in Table 3, with an increase in the temperature of sample processing the value of Ss LAHL increases from 2.6 to 27.9 m²/g, i.e. 10.7 times. Obviously, this is due to a change in the shape and size of particles and an increase in the porosity of samples.

Scanning electron microscopy was used to obtain images of the surface microlrelief of LAHL particles (Fig. 2).

During heat treatment, not only the total number of pores increases, but the pore size distribution also changes (Fig. 1).
At the same time, the main pore size of these samples corresponds to the diameter: for LAHL initial – 51.4 nm, for LAHL 150 – 23.9 nm, for LAHL 250 – 142.3 nm.

From the micrographs presented in Fig. 2 we can see that with an increase in heat treatment temperature, the surface of CTW particles becomes more prominent, developed, the number of pores, cavities, irregularities increases, and the overall surface roughness and its unsoundness increase.

A visual assessment of the material showed that after 300 °C, intensive carbonization of the material begins, and at a temperature of 400 °C, a significant part of the leaves turns into ashes.

The results of derivatographic analysis (Fig. 3) clarified visual observations. In the temperature range from 100 to 260 °C, the removal of bound moisture and the decomposition of tannins occur. At a temperature of 260-270 °C, exothermic processes are gradually intensified and the first peak of thermal emission falls at 337.3 °C.

According to literature data [24, 25], decarbonylation and decarboxylation processes take place in this temperature range, the formation of levoglucosane occurs by breaking the glucosidic bond in the macromolecule of cellulose and the subsequent intramolecular rearrangement in elementary units.

### TABLE IV. PERCENTAGE OF CHEMICAL ELEMENTS IN LAHL AT DIFFERENT PROCESSING TEMPERATURES

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaves, initial</td>
<td>60.19</td>
<td>32.71</td>
<td>0.08</td>
<td>0.24</td>
<td>0.31</td>
<td>2.06</td>
<td>0.16</td>
<td>0.18</td>
<td>0.51</td>
<td>1.11</td>
<td>2.00</td>
<td>0.45</td>
</tr>
<tr>
<td>Leaves 250 ℃</td>
<td>62.27</td>
<td>26.05</td>
<td>0.22</td>
<td>0.44</td>
<td>0.21</td>
<td>1.80</td>
<td>0.22</td>
<td>0.24</td>
<td>1.15</td>
<td>2.30</td>
<td>4.82</td>
<td>0.28</td>
</tr>
<tr>
<td>Leaves 500 ℃</td>
<td>10.57</td>
<td>41.09</td>
<td>0.96</td>
<td>2.04</td>
<td>1.11</td>
<td>10.00</td>
<td>1.17</td>
<td>0.64</td>
<td>4.21</td>
<td>5.37</td>
<td>21.77</td>
<td>1.08</td>
</tr>
</tbody>
</table>

![Fig. 1](image1.png) Change in the distribution of pore size depending on the firing temperature LAHL: a – 50 ℃, b – 150 ℃, c – 250 ℃.

![Fig. 2](image2.png) Micrographs of LAHL surface: a – 50 ℃, b – 150 ℃, c – 250 ℃.
The highest thermal effect corresponds to the temperature of 463.9 °C, which indicates the processes of dehydrogenation and methane release [24].

As a result of heat treatment of the cellulose-containing material, the percentage of chemical elements changes (Table 4). As it can be seen from the data presented, LAHL250 contains the highest carbon content of the studied samples, which is explained by high content of cellulose and other organic components of the leaf together with the removal of adsorbed moisture.

To determine the optimal temperature of the plant waste modification, model emulsions containing industrial oil with a concentration of 0.1 g/dm³ were subjected to purification. 0.2 g of LAHL, heat-treated in the temperature range of 100-300 °C, was added to 0.1 dm³ of the oil-containing emulsion.

The effect of LAHL heat treatment temperature on the cleaning efficiency is shown in Fig. 4. As it can be seen in Fig. 4, high purification efficiency (91 and 97%) is achieved even at a heat treatment temperature of 150 and 250 °C, respectively. With further increase in temperature the purification efficiency practically does not increase. Therefore, increasing the baking temperature is impractical.

The sorption material obtained by heat treatment is effective against petroleum products in aqueous media.

**Acknowledgment**

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**References**


IV. CONCLUSION

Data were obtained on the peculiarities of temperature modification of horse chestnut leaves in order to obtain a sorption material for the purification of waste water from petroleum products.

It is established that the optimal modification temperature is 250 °C, while the surface of the particles of chestnut leaves becomes more prominent, developed, the number of pores, cavities, irregularities increases, the total surface roughness and its unsoundness increase. At higher temperatures, cellulose and levoglucosane are decomposed with a decrease in the total percentage of carbon from 62 to 10 wt. %

High purification efficiency of model emulsions containing industrial oil (91 and 97%) is achieved even at a heat treatment temperature of 150 and 250 °C, respectively. With further increase in temperature the purification efficiency practically does not increase. Therefore, increasing the baking temperature is impractical.

The sorption material obtained by heat treatment is effective against petroleum products in aqueous media.


