Modification of Chestnut Leaf Litter for Application in Water Treatment

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Abstract. The effect of the temperature of heat treatment of chestnut tree waste (CTW) on the turbidity of oil-containing emulsions was studied. A granulometric analysis of the dispersity of particles of heat-treated CTW was carried out. In the experiments, the influence of the heat treatment temperature of the TW on the decrease in the turbidity of the model emulsions of spindle oil was determined. Sorption and desorption isotherms are constructed. Mixing of the sorption material with the model emulsion was carried out with a laboratory mixer for 24 hours. Initial parameters: solution temperature 25 °C, sorbent quantity 3 g / dm³. The maximum sorption capacity of CTWT relative to spindle oil, according to the results of the studies, was 370 mg / g.

1. Introduction

Today the oil industry is leading for the world economy. Nowadays, oil and oil products (OP) are the most common pollutants in the World Ocean. They fall into the environment during oil production, oil transportation and oil refining. Large masses of OP fall into the World Ocean in due to tanker accidents, gusts of pipelines, etc. [1, 2].

In Table 1, the distribution of the contribution to the pollution of the world ocean by oil from various sources is shown [3].

| Source of pollution                          | Quantity, mln.t / year | Share, %   |
|---------------------------------------------|------------------------|------------|
| Transportation, including                   | 2.13                   | 34.9       |
| - ordinary transportation / catastrophe     | 1.83 / 0.3             | 30.0 / 4.9 |
| Removal by rivers                           | 1.9                    | 31.1       |
| Atmospheric impact                          | 0.6                    | 9.8        |
| Natural sources                             | 0.6                    | 9.8        |
| Industrial wastes                            | 0.3                    | 4.9        |
| Urban wastes                                 | 0.3                    | 4.9        |
| Waste from coastal oil refineries           | 0.2                    | 3.3        |
| Oil production in the high seas, including: | 0.08                   | 1.3        |
| - Ordinary operations                       | 0.02                   | 0.3        |
| - Accident                                  | 0.06                   | 1.0        |
The influence of oil and oil products on aquatic ecosystems and the state of hydrobionts can be seen in the form of a direct change in the habitat, poisoning of living organisms, a violation of their physiological activity [4, 5].

Oil pollution of the world ocean is spread all over the globe. From 2 to 4% of the water surface of the Pacific and the Atlantic Oceans is constantly covered with oil film. Sea waters are annually supplied by up to 6 million tons of oil hydrocarbons. Continental oil pollution enters the ocean through the river runoff [6]. The rivers of the world each year carry more than 1.8 million tons of oil products into the sea and ocean waters [7].

2. Relevance
The treatment of wastewater containing various OP presents a complex problem. Various methods are used for this purpose: mechanical, chemical, physicochemical, reagent, biological ones [8]. One of the most widespread and effective ways to treat sewage from the OP is sorption. Advantages of the adsorption method are high efficiency, as well as the possibility of purification of sewage containing several substances. The degree of adsorption purification reaches 95% and depends on the chemical nature of the substances [9, 10], the adsorbent, the area of the adsorption surface and its availability [11]. It should be noted that adsorbents are able to extract organic contaminants from water, which are not usually extracted by others, for example, by biological methods [12].

Researches in the field of sorption purification of water are conducted both in the direction of improving the structure of the sorption surface and in the search for new, cheap and efficient sorbents, especially on the basis of industrial wastes [13].

Activated carbon, coke fines, peat, coal, sawdust, ash, various synthetic materials are often used as sorbents [14, 15].

Along with cellulose-containing waste (sawdust, bark), tree waste (TW) of various tree species is a very promising sorption material [16, 17]. According to estimates of domestic and foreign scientists, the amount of TW in coniferous forests is 54-78%, in leaf forests - 83%, from 2.51-7.76 t / ha of total annual tree waste quantity [18]. Every autumn, thousands of tons of TW are exported from the territory of the cities of the Russian Federation and are buried at landfills. From the point of view of rational use of natural resources such treatment with promising sorption material is economically and environmentally unjustified.

Thus, the use of TW in the sorption purification of oily wastewater is promising and effective from the point of view of rational use of natural resources.

3. Formulation of the problem
The objectives of this research are:
- carrying out modification of TW for improvement of sorption properties;
- determination of the effect of heat treatment of TW on the reduction of turbidity and increase in the efficiency of cleaning oily wastewater.

4. Research results
We used spindle oil brand I-20A, \( \rho = 890 \text{ kg} / \text{m}^3 \) at 20 °C [19].

Spindle oil is a low-viscosity distillate oil from low-hardening oils, which has a good viscosity-temperature characteristic and high anticorrosive properties. This type of oil is used as a working mass for hydraulic systems of diverse industrial machines and mechanisms that are designed for operation under conditions of high speed and medium loads. Such mechanisms and systems include rolling and sliding bearings, lightly loaded bushes, small and medium-loaded gears, individual units of knitting, sewing machines etc. The chosen type of oil can also serve as a raw material base for the production of special-purpose lubricants and a component for lubricating fluids of industrial machines. Due to its properties, spindle oil guarantees optimal operation of hydraulic drives in a wide range of temperatures: -35 °C to 100 °C, therefore it is widely used. Spilled oil enters waste water during operation and cleaning of equipment [20]. The ground natural and heat-treated chestnut tree waste
(CTW), collected in the territory of the city of Belgorod was used for extraction from water emulsions of spindle oil. For cleaning, TW and heat-treated TW (HTW) were used. Emulsions of spindle oil were prepared by dilution with tap water. The volume of model solutions taken for purification was 100 ml, the contact time of HTW with model solutions was 20 min, and the temperature was 20 °C. The heat treatment of ground CTW was carried out at temperatures ranging from 105 to 650 °C in a Liop LF-7/13-G2 muffle furnace in within 20 minutes.

The graphs of the results of laser granulometric analysis of the dispersion of CTW particles heat-treated at temperatures of 300 °C and 650 °C (Fig. 1) show that heat treatment under experimental conditions has practically no effect on the dispersion of the material. In the experiments, the influence of the heat treatment temperature of the TW on the decrease in the turbidity of the model emulsions of spindle oil was determined. The turbidity of the emulsions before and after purification in units of the NTU (Nephelometric Turbidity Unit) was determined using a turbidimeter HI 98703 [21]. On the graph in the coordinates NTU = f (t burn.), shown in Fig. 2, it is evident that when the heat treatment temperature of TW increases, the turbidity of the model emulsion after purification reduces to a greater extent than when using CTW heat treated at lower temperatures. So, with the initial value of the NTU model emulsion of 670 units, the decrease in turbidity for TW treated at 105 °C was only 58%, and with the TWT obtained at 300 °C, the decrease in NTU was already 97.8 %. With a further increase in the heat treatment temperature, the decrease in the NTU values is not so intensive, which probably can be explained by the high sorption properties of TWT already acquired at t = 300 °C.

The influence of the heat treatment temperature of the CTW on the efficiency of extraction of spindle oil from aqueous emulsions is shown in Fig. 3.

![Figure 1](image1.png)

**Figure 1.** Integral and differential distribution of particle size CTWT at: a) 300 °C; b) 650 °C.

![Figure 2](image2.png)

**Figure 2.** Influence of the burning temperature of the TW on the turbidity of the model emulsion.

![Figure 3](image3.png)

**Figure 3.** Influence of the heat treatment temperature of the CTWT on the efficiency of cleaning the model emulsion.
The adsorption kinetics of the oil-containing emulsion with the sorption material CTWT was studied in the single-stage static adsorption regime. Mixing of the sorption material with the model emulsion was carried out with a laboratory mixer for 24 hours. Initial parameters: solution temperature 25 °C, sorbent quantity 3 g / dm$^3$. The isotherms of sorption and desorption of the model emulsion are shown in Fig. 4.

![Figure 4. Sorption-desorption isotherms of the model emulsion: - desorption - sorption](image)

The sorption isotherm, shown in Fig. 4, corresponds to the I type of adsorption isotherms and describes the monomolecular adsorption on the CTWT surface. The maximum sorption capacity of CTWT relative to spindle oil, according to the results of the studies, was 370 mg / g or 0.37 g / g. The location of the desorption isotherm in the immediate vicinity of the 0-X axis indicates the character of the nature of the adsorption process, which is close to the specific one. In this case, hydrophobic interaction probably produces adsorption.

5. Conclusions
Thus, the results of the conducted studies have proved the possibility of using chestnut tree waste as a sorption material for removing emulsified spindle oil from aqueous media. It has been established that the sorption capacity of heat treated tree waste with respect to spindle oil is 370 mg / g.

6. References
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