Research of Mixed Carbon Sorbents for Removal of Oil Products from Water and Soil for Preservation of Environmental Infrastructure

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Abstract. The article presents the results of studies on the study of technologies for obtaining carbon sorbents from by-products of agriculture, woodworking industry and utilities under the influence of low-temperature one-stage carbonization, as well as structural, physicochemical, absorbing properties of mixed carbon-carbon and carbon-mineral sorbents and their effectiveness and economic feasibility in removing petroleum products from the environment and preserving its infrastructure. Oil consumption and absorption capacity of petroleum products of the mixture of pine sawdust carbonate: expanded graphite, at a ratio of 50:50%, 2.5-3.0 times higher than the sawdust carbonate. Its use is the most promising and cost-effective in removing petroleum products from the environment and preserving environmental infrastructure. The obtained data on influence of the qualitative composition of mixed materials on their sorption capacity in relation to oil and oil products allow us to suggest the feasibility of using carbon-carbon materials as effective sorbents of oil products from water and soil, and carbon-mineral, for example, as effective barriers to preventing the migration of oil and petroleum products into groundwater. Carbon-carbon materials should be used as effective sorbents to remove petroleum products from the water surface and soil, and carbon-mineral as effective barriers to prevent the migration of oil and petroleum products into groundwater.

1. Introduction
Fuels and lubricants, even with careful storage and use in large quantities, enter the environment causing significant environmental damage [1]. Various methods are used to clean water bodies [2] and soils from oil [3] and oil products [4]. The most widely used in practice method of purification from petroleum products – absorption (sorption) [5]. Recently, mixed carbon-carbon [6] and carbon-mineral sorbents have been widely used to remove petroleum products from the environment [7] and preserve the infrastructure of the environment [8]. Mixed are mixtures obtained from two or more individually pure sorbents, which acquire different properties from the source materials [9]. The structural-sorption
properties of mixed sorbents are not a simple set of properties of the source components [10], there is always more or less deviation from the original analogues [11], and, in some cases, the resulting sorbent may acquire completely new properties [12]. The need for the use of mixed sorbents is associated with: reducing the use of more expensive (due to the cost of carbonization) carbon sorbents [13]; limited amount, in certain areas, of raw materials for carbon sorbents [14]; reduction of energy costs; obtaining cheaper sorbents [15]; improvement of sorption and technical and economic indicators; efficiency and success of removal of oil products from the environment [16]; relevance of environmental quality monitoring [17]. Petroleum products are common pollutants in the biosphere [18]. Once they enter the environment, as a result of chemical and biological decomposition, harmful toxic substances are formed, which also have a negative impact on living organisms [18]. Studies of carbonization processes, taking into account the nature and structure of raw materials, aimed at obtaining effective sorbents with high sorption capacity and absorption capacity of petroleum products are important [19]. Obtaining and determining the system of the most efficient use of mixed carbon-carbon and carbon-mineral sorbents [20], taking into account their physical and chemical, structural-sorption characteristics [21], in comparison with the relevant indicators of raw materials [22], for removal of petroleum products from the environment and preservation of environmental infrastructure, has important scientific [23] and practical significance and needs further research [24].

2. Purpose of research
The purpose of our research was to study technologies for obtaining carbon sorbents from by-products of agriculture, woodworking industry and utilities under the influence of low-temperature single-stage carbonization, as well as structural, physicochemical, absorption properties of mixed carbon-carbon and carbon-mineral and carbon-mineral economic feasibility in the removal of petroleum products from the environment and the preservation of environmental infrastructure.

3. Materials and methods
The use of carbon materials in vegetable raw materials is becoming more common due to their high sorption properties. The indicators characterizing sorbents of carbon origin, first of all, are defined both by the nature of initial raw materials, and conditions of their reception. We studied the structural and absorption characteristics of sorbents for the removal of petroleum products and the preservation of environmental infrastructure: plant origin; carbon sorbents based on vegetable raw materials obtained under the influence of low-temperature one-stage carbonization on the raw material; mixed carbon-carbon and carbon-mineral sorbents. The study of the process of carbonization of sawdust of coniferous trees (pine) revealed that at each studied carbonization temperature we have the optimal value of its duration, at which the oil content of carbonate is maximum, as shown in figure 1.

![Figure 1](image.png)

**Figure 1.** Dependence of oil content of carbon materials a (g/g) from pine sawdust on time τ (min) and temperature of carbonization $T_k (^\circ\text{C})$. 
The appearance of maxima in figure 1 can be explained by the change in the porous structure and surface chemistry of carbon materials during carbonization. Thus, at the initial stage of the process of carbonization of pine sawdust (up to 350 °C), due to the removal of moisture, volatile and resinous components, pores are formed, which leads to an increase in its sorption capacity for oil and petroleum products to some maximum value. Further carbonization (350-450 °C) leads to carbon burnout and, consequently, an increase in the number of macro pores, which changes the structure of carbonates in the direction of reducing mesoporosity. As you can see, under the influence of temperature, the porous structure is partially degraded, which leads to a decrease in the sorption capacity of the carbonate. The optimal mode of carbonization of pine sawdust is 300°C (±10°C) and a time of 8-10 minutes, which is confirmed by the data in table 1.

Table 1. Change in the structural and sorption characteristics of carbon materials from pine sawdust depending on the conditions of heat treatment.

| T_c (°C) | τ (min) | V_s (C_6H_6), (cm^3/g) | A(ESR) (mg-ec/g) |
|----------|---------|------------------------|-----------------|
| 250      | 5       | 0.08                   | 1.5             |
| 250      | 10      | 0.10                   | 2.6             |
| 250      | 15      | 0.09                   | 1.7             |
| 300      | 5       | 0.09                   | 1.8             |
| 300      | 10      | 0.10                   | 3.6             |
| 300      | 15      | 0.07                   | 2.4             |
| 350      | 5       | 0.07                   | 2.3             |
| 350      | 10      | 0.06                   | 2.5             |
| 350      | 15      | 0.06                   | 1.7             |
| 400      | 5       | 0.06                   | 2.3             |
| 400      | 10      | 0.05                   | 1.9             |
| 400      | 15      | 0.04                   | 1.6             |

In the case of purification of oil and petroleum products from water, mainly from its surface, an important characteristic of the sorbent is buoyancy. Because, at loss of buoyancy, in the presence of oil agglomerates the bottom of reservoirs is polluted and repeated pollution of a surface of water in case of desorption of oil is possible. We conducted studies of carbonates for buoyancy, obtained at different values of temperature and heat treatment time, depending on the duration of their stay on the water surface. Mixed carbon-carbon sorbents are obtained by mechanical mixing of carbon materials in certain predetermined ratios. Obtaining mixed sorbents using, as one of the components, pine sawdust carbonate (as a base), which has the best sorption properties compared to other sorbents, with optimal carbonization parameters, allows you to have cheaper sorbents due to lower energy costs.

The structural sorption capacity of various mixed carbon-carbon sorbents, based on vegetable raw materials, which have the most widespread use for purification from petroleum products, as well as carbon-mineral sorbents was investigated. The following carbon-carbon sorbents have been proposed.

Pine sawdust carbonate: walnut sawdust carbonate (optimal carbonization conditions) in percentage 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90; expanded graphite in the percentage 90:10, 80:20, 70:30, 60:40, 50:50, 40:60; since the expanded graphite has a fairly low bulk density (0.012 g/cm^3), the percentage of 30:70, 20:80, 10:90 should not be used; rapeseed straw carbonate (optimal carbonization conditions) in a percentage ratio of 50:50.

Carbon-carbon sorbents, within one mixture, differ from each other only in the ratio of components. Mixed carbon-mineral sorbents were obtained by mechanical mixing of carbon and mineral components in certain predetermined ratios. The value of the sorption capacity of natural mineral materials in relation to oil and oil products decreases in the following series: saponite → ash → bentonite → crucible → clinoptilolite. Using pine sawdust, with optimal carbonization
parameters, having high values of sorption capacity and natural sorbents, carbon-mineral sorbents were obtained: saponite, ash, bentonite; in percentage 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90. Mixed sorbents are a mixture of two individually pure materials. The determined structural sorption characteristics of mixed sorbents were compared with the corresponding additive values calculated on the basis of the known composition of the sorbent. Structural and sorption characteristics of mixed materials are not a simple sum of the properties of the original components, there is always a deviation from the additivity.

4. Results and discussion

Structural-sorption and physico-chemical characteristics of mixed carbon-carbon materials change with the change of mass fraction of components in the composition of the mixture. Thus, \( V_s \) and \( A(ESR) \) capacity of petroleum products for carbon-carbon sorbents increase and reach a maximum at a ratio of components close to 50:50% of the mass (figure 2).

![Figure 2. Dependence of the value of the exchange capacity on the composition of carbon-carbon mixtures (pine sawdust carbonate: expanded graphite).](image)

Theoretical (calculated) values of the sorption capacity were obtained based on the actual values of each sorbent and its mass fraction in the composite mixture. Manifestation of the synergistic effect in the mixed material, apparently, is a consequence of the determining role of the surface chemistry of carbon materials of plant origin, as the static exchange capacity of graphite in comparison with carbon sorbents are quite low. A further reduction in the size of the synergistic effect is due to a reduction in the carbon sorbent content of the mixture. The manifestation of the synergistic effect in the case of the sorption volume of the pores of mixed carbon-carbon sorbents is due to both the porous surface of carbon materials of plant origin and the sorption volume of the pores of expanded graphite. Since the expanded graphite has a low value of bulk density (0.012 g/cm\(^3\)), the further decrease in the size of the synergistic effect is associated with a decrease in the content of expanded graphite in the mixture.

Inadequate nature of sorption of oil and oil products is observed, first of all, on carbon-carbon sorbents of mixed type. Oil consumption increases with the change in the ratio of components in materials of mixed type and reaches a maximum at such values at which the maximum \( ESR \) and sorption volume of the pores are observed. Oil capacity and absorption capacity of petroleum products of pine sawdust carbonate: expanded graphite, at a ratio (within 50:50%), 2.5-3.0 times higher than the capacity of pine sawdust carbonate, which makes it extremely effective and promising in use for cleaning from petroleum products of the environment and preservation of environmental infrastructure. Therefore, the combination of sorption pore volume (due to expanded graphite) and high exchange capacity (due to pine sawdust carbonate) can cause a high value of oil-carbon-carbon mixed materials. Mixtures of expanded graphite with sawdust carbonates of other trees or straw have high sorption properties. They have higher sorption rates compared to the source materials, so in the absence of sawdust from coniferous trees, you can use to make a carbon-carbon mixture of expanded graphite and carbonates from sawdust from other trees or straw.

Manifestation of antisynergistic effect in the case of sorption volume of pores and \( A(ESR) \) of mixed carbon-mineral sorbents is due to changes in the nature of active centers, namely, by reducing the
content of carbon components in the mixture (figure 3). The obtained mixed carbon-mineral materials were investigated for buoyancy. It turned out that the mineral component (saponite) sinks when it is on the surface of the water for one hour, the carbon component has a buoyancy of 99% for 6 months. Therefore, as the ratio of the mass fraction of the components in the mixture changes and buoyancy. As the mineral component in the mixture increases, the buoyancy of the obtained materials decreases.

Inadequate nature of sorption of petroleum products is also observed on carbon-mineral sorbents of mixed type. The oil content decreases as the ratio of components in materials of mixed type changes and reaches a minimum at such values at which the minimum value of \( (ESR) \) and the volume of sorption pores are observed. The manifestation of the antisynergistic effect in the case of mixed carbon-mineral materials is due to a change in the nature of the active centers, namely, by reducing the content of the carbon component in the mixture.

![Figure 3](image)

**Figure 3.** Dependence of the value of the sorption volume of the pores and the exchange capacity on the composition of the carbon-mineral mixture (pine sawdust carbonate: saponite).

The obtained data on the influence of the qualitative composition of mixed materials on their sorption capacity in relation to oil and oil products allow us to suggest the feasibility of using carbon-carbon materials as effective sorbents of oil products from water and soil, and carbon-mineral, for example, as effective barriers to preventing the migration of oil and petroleum products into groundwater. Carbon-carbon sorbents (one of the components of which, pine sawdust carbonate (basic), as it has the best sorption properties) have better sorption and absorption properties, relative to the corresponding indicators of the materials that are part of them.

5. **Conclusions**

1. Oil content and absorption capacity of petroleum products of pine sawdust carbonate: expanded graphite, at a ratio (within 50:50%), 2.5-3.0 times higher than pine sawdust carbonate. Its use is the most promising and cost-effective in removing petroleum products from the environment and preserving environmental infrastructure.

2. Carbon-carbon materials should be used as effective sorbents to remove petroleum products from the water surface and soil, and carbon-mineral as effective barriers to prevent the migration of oil and petroleum products into groundwater.

6. **References**

[1] Kovalenko О, Novoseltseva V and Kovalenko N 2018 Biosorbents – prospective materials for heavy metal ions extraction from wastewater *Food Science and Technology* 12(1) 118-22

[2] Hassan A 2019 Review of the global oil and gas industry: a concise journey from ancient time to modern world *Petroleum Technology Development Journal* 3(2) 123-41
[3] Melbert A A, Shaposhnikov Y A, Mashensky A V and Voinash S A 2019 Effects of 8412/12 catalytic converter prestarting on harmful emissions at negative ambient temperatures Journal of Physics 1177 012011

[4] Diemer R 2019 Transport in the European Union – current trends and issues Mobility and Transport B-1049 143-91

[5] Mohan D, Pittman C U and Steele P H 2006 Pyrolysis of wood/biomass for bio-oil: a critical review Energy and Fuels 20(3) 848-89

[6] Rogovskii I L, Kalivshcko S M, Voinash S A, Korshunova E E, Sokolova V A, Obukhova I A and Kebko V D 2020 Research of absorbing properties of carbon sorbents for purification of aquatic environment from oil products IOP Conference Series: Earth and Environmental Science 548 062040

[7] Morteza A, Mohammad Reza Masnavi M R and Khalighi N 2012 Use of natural purification of water cycle and water management as a solution towards eco-design Design for Innovative Value Towards a Sustainable Society 7 6-18

[8] Hrynkiv A, Rogovskii I, Aulin V, Lysenko S, Titova L, Zagurskiy O and Kolosok I 2020 Development of a system for determining the informativeness of the diagnosing parameters of the cylinder-piston group of the diesel engines in operation Eastern-European Journal of Enterprise Technologies 3(105) 19-29

[9] Azat S, Pavlenko V V, Kerimkulova A R and Mansurov Z A 2012 Synthesis and structure determination of carbonized nano mesoporous materials based on vegetable raw materials Advanced Materials Research 535 1041-5

[10] Rogovskii I L, Titova L L, Trokhaniak V I, Marinina L I, Lavrinenko O T and Bannyi O O 2020 Engineering management of machine for formation of artificial shell on seed vegetable cultures INMATEH Agricultural Engineering 848 74-77

[11] Cruz J F, Matejova L, Pirilä M, Ainasaari V, Canepa C and Mousavi S M 2015 A comparative study on activated carbons derived from a broad range of agro-industrial wastes in removal of large-molecular-size organic pollutants in aqueous phase (water, air, and soil pollution) Water Air and Soil Pollution 226(11) 213-35

[12] Rogovskii I, Titova L, Novitskii A and Rebenko V 2019 Research of vibroacoustic diagnostics of fuel system of engines of combine harvesters Engineering for Rural Development 18 291-8

[13] Koumanova B 2006 Fate of chemicals in the aquatic environment Chemicals as Intentional and Accidental Global Environmental Threats XVIII 93-103

[14] Ngene S, Tota-Maharaj K, Eke P and Hills C 2016 Environmental and economic impacts of crude oil and natural gas production in developing countries International Journal of Economics, Energy and Environment 1(3) 64-73

[15] Widner K, Naisse C, Rumpel C and Glaser B 2013 Chemical modification of biomass residues during hydrothermal carbonization Organic Geochemistry 54 91-100

[16] Coq L L and Duga A 2012 Syngas treatment unit for small scale gasification-application to is engine gas quality requirement Journal of Applied Fluid Mechanics 5(1) 95-103

[17] Dias J M, Alvim-Ferraz M, Almeida M F, Rivera-Utrilla J and Sánchez-Polo M 2007 Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review Journal of Environmental Management 85(4) 833-46

[18] Rogovskii I, Titova L, Trokhaniak V, Trokhaniak O and Stepanenko S 2020 Experimental study of the process of grain cleaning in a vibro-pneumatic resistant separator with passive weeders Bulletin of the Transilvania University of Brasov Series II: Forestry Wood Industry Agricultural Food Engineering 13(62) 117-28

[19] Sun Y and Webley P A 2010 Preparation of activated carbons from corncob with large specific surface area by a variety of chemical activators and their application in gas storage Chemical Engineering Journal 162(3) 883-92
[20] Ahmad F, Daud W W, Ahmad M A and Radzi R 2012 Shell-based activated carbon by CO$_2$ activation in removing of cationic dye from aqueous solution: kinetics and equilibrium studies Chemical Engineering Research and Design 90(10) 1480-1490

[21] Nieto-Delgado C and Rangel-Mendez J R 2013 In situ transformation of agave bagasse into activated carbon by use of an environmental scanning electron microscope Microporous and Mesoporous Materials 167 249-53

[22] Haiping Y, Yan R, Chen H and Zheng C 2007 Characteristics of hemicellulose, cellulose and lignin pyrolysis Fuel Journal 86(12-13) 1781-8

[23] Klavins M and Porshnov D 2013 Development of a new peat-based oil sorbent using peat pyrolysis Environmental Technology 34(9-12) 1577-82

[24] Zhao X and Zhu S 2012 Prediction of water breakthrough time for oil wells in low-permeability bottom water reservoirs with barrier Petroleum Exploration and Development 39(4) 504–7