Research of absorbing properties of carbon sorbents for purification of aquatic environment from oil products

I L Rogovskii¹, S M Kalivoshko¹, S A Voinash², E E Korshunova³, V A Sokolova⁴, I A Obukhova⁴ and V D Kebko⁴

¹National University of Life and Environmental Sciences of Ukraine, 15, Heroiv Oborony str., Kyiv, 03041, Ukraine
²Federal State Budgetary Educational Institution of Higher Education "Novosibirsk State Agrarian University", 160 Dobrolyubova str., Novosibirsk, 630039, Russian Federation
³Federal State Budgetary Educational Institution of Higher Education "Altai State University", 61, Avenue Lenin, Barnaul, 656049, Russian Federation
⁴Federal State Budgetary Educational Institution of Higher Education “St. Petersburg State Forestry University named after S.M. Kirov”, Institutskiy Per. 5, Saint-Petersburg, 194021, Russian Federation

³E-mail: sergey_voi@mail.ru

Abstract. The article presents the results of the study of structural-sorption performance and absorption properties of both raw materials and carbon sorbents obtained in the carbonization process, in terms of their ability to absorb petroleum products from water and contribute to the preservation of environmental infrastructure. Under the proposed mode of carbonization received hydrophobic sorbents. The analysis of the obtained results shows that carbon materials based on pine sawdust, obtained at a temperature of 300 °C for 8-10 minutes, have the best buoyancy – 97-100%. This can be explained by the fact that in the process of carbonization of cellulose-containing raw materials the last of the components of plant tissues decomposes lignin (active decomposition of lignin occurs in the temperature range 280-325 °C). As a result of research it is established that in the process of low-temperature one-stage carbonization of vegetable raw materials unauthorized hydrophobization of the sorbent surface is carried out. For fast and efficient collection of oil and oil products, the sorbent must have the maximum sorption rate, which will reduce the absorption time of pollutants. The highest sorption rate is shown by a mixture of pine sawdust carbonate: expanded graphite (50:50) and carbon material based on pine sawdust, which can be explained by the developed porous structure and surface chemistry of the materials.

1. Introduction

In the world uses large quantities of petroleum, important among which is the petroleum products to meet energy needs [1]. The use of fuel and lubricants, through primarily an increase in the number of vehicles [2], the way in Europe, in contrast to our state, growing spread acquire electric vehicles increases, which increases the load on the environment and its infrastructure [3].

Petroleum products, which are used, are current or potential polluters of air, water, soil, infrastructure and the environment in general [4]. The adverse effects of combustive-lubricating materials released...
into the environment, a responsible process and depends on the choice of technologies, techniques and methods. For water purification, as a special ecological system, from oil and oil products using many methods [5]. Widespread method of cleaning from oil products based on the processes of absorption (sorption). Sorption is able to provide, at a relatively low cost, deep cleaning from oil products, without the use of chemicals to the aquatic environment [6].

Among a large number of sorbent substances has an important role to carbon adsorbents, obtained by carbonization, based on vegetable raw materials [7]. Among their advantages are simplicity, accessibility, efficiency and relative cheapness. Raw material for the synthesis of carbon sorbents can be used for many tonnes waste of woodworking industry (sawdust, shavings), agricultural activities (straw, chaff) and utilities (leaves of trees) [8]. The prospect of their use as sources of raw materials for the synthesis of carbon sorbents is not limited. However, such sorbents studied, yet not fully, and therefore they require further research, indicating the relevance of this topic.

Fuel and lubricants are quite common pollutants of the biosphere [9]. They are also harmful hydrocarbons of different classes, contains certain impurities which can form complex compounds with heavy metals [10]. If oil gets into the water, the result of biological degradation and chemical reactions may form toxic substances, which adversely affect biological organisms [11]. The study of the processes of carbonization, when the raw material is a by-product of wood, agricultural and municipal production necessary for high-performance sorbents with high sorption absorption capacity of oil, trapped in the water, require further attention and research [12].

Obtaining carbon sorbents was carried out by carbonization by-products of woodworking industry, agriculture and public services. Carbonation is a method of obtaining carbon sorbents from vegetable raw materials have sorption properties [13], which starts by heating the feedstock to above 100 °C.

As used cellulose pulp materials, the carbonization processes of destruction of polymer chains with the release of large amounts of volatile compounds and resinous substances of the complex structure [14]. Transform the structure of cellulose and lignin, in the process of carbonization at different temperatures, comprises the following steps [15]:

1) to 150 °C – desorption of physically adsorbed water (weight loss of up to 15 %). Additionally, the possible beginning of dehydration due to the formation of water from groups of OH and H that are linked by hydrogen bonds;
2) 150-240 °C – basic process – internally molecular dehydration with the formation of bonds \(-C=O\) and \(-C=O\);
3) 240-400 °C – basic process – degradation of macromolecules as a result of intensive destruction of 1.4 glycoside bond, cyclic \(-C-O-C\) and part of \(-C=O\) bonds by a radical mechanism;
4) 400-700 °C – basic process – aromatization with the release of \(H_2\) and burnout and condensation of the fragments of \(C_i\) in turbostation the carbon layer.

The carbonization process starts at temperatures above 100 °C [16]. Within the temperature range of 250-300 °C are the main the decomposition reaction is accompanied by release of carbon monoxide and carbon dioxide liquefied mixture consisting of acetic acid, its derivatives and methanol, and finally the lungs of tar and heavy. At temperatures above 300 °C is a small selection of heavy tars and gases: \(CO_2\) and \(CO\) [14].

Consequently, together with the carbonization processes of destruction of polymer chains with the simpler emission of volatile compounds and resinous substances, a complex structure, resulting in the development of the porous structure [18]. The development of the porous structure due to burnout of individual areas and arisemendy products, distinguished primarily by water vapour and carbon dioxide. Create pores in a solid body, a significant inner surface, and hence the specific surface area. Developed specific surface area ensures the availability of functional groups and the rate processes that occur on it.

For different stages of the carbonization process, the value of activation energy varies in different temperature zones the decomposition of the various components of plant tissues. In the first place, breaks down the hemicellulose, then cellulose and lignin. During the carbonization of vegetable raw materials, the processes of destruction of polymer chains with the release of volatile simple compounds (carbon monoxide (II), carbon dioxide, hydrocarbons of saturated, unsaturated and aromatic series, ketones,
aldehydes, alcohols and organic acids), as well as resinous substances, and mesoporous in the form of craters and cracks, resulting in the development of a porous structure.

Adherence to these parameters allowed to develop a new method of obtaining carbon-absorbing sorbents based on heat treatment of vegetable raw materials in low-temperature single-stage mode [19]. Indicators that characterize the obtained carbon sorbents depend on both the raw material and the conditions of their production [20]. We investigated the structural sorption parameters and absorption properties of both raw materials and carbon sorbents obtained in the carbonization process, in relation to their ability to absorb petroleum products from water and to help preserve the infrastructure of the environment.

2. The aim of research
The aim of our research was to study the physicochemical, structural and absorption properties of carbon sorbents, technology for their production, by-products of woodworking industry, agriculture and utilities, by heat treatment and efficient use in removing petroleum products from the aquatic environment using environmental infrastructure.

3. Materials and methods
Structural characteristics, sorption and absorption properties were investigated by the following indicators: \( A(ESR) \) — sorption capacity (sorption value); \( V_e \) — sorption volume of pores; \( \Delta \) — bulk density; \( S_p \) — specific surface area; \( \alpha \) — oil (patrol, diesel, oil, kerosene) consumption, g/g. Which were determined by the formulas:

\[
A(ESR) = (c_0 - c_p) \cdot V_1 \cdot (m_c \cdot 1000)^{-1}, \text{mg- eq/g}
\]  

where: \( c_0 \) — initial concentration, mg- eq/cm\(^3\); \( c_p \) — equilibrium concentration, mg- eq/cm\(^3\); \( V_1 \) — volume of solution, cm\(^3\); \( m_c \) — mass of sorbent, g;

\[
V_e = \Delta q \cdot (q_0 \cdot \rho_b)^{-1}, \text{cm}^3/g
\]  

where: \( q_0 \) — the initial mass of the sorbent, g; \( \Delta q \) — the increase in the mass of the sorbent, g; \( \rho_b \) — density of benzene at room temperature (0.875 g/cm\(^3\)).

\[
\Delta = (M_{ms} - M_{ec}) \cdot V_2^{-1}, \text{g/cm}^3
\]  

where: \( M_{ec} \) — the mass of the empty cylinder, g; \( M_{ms} \) — mass of the cylinder with sorbent, g; \( V_2 \) — the volume of the cylinder, cm\(^3\).

\[
S_p = K \cdot S_A \cdot m_c^{-1}, \text{m}^2/g
\]  

where: \( m_c \) — the mass of the sorbent, g; \( K \) — installation constant; \( S_A \) — the integrated area of the chromatographic peak, m\(^2\).

\[
\alpha = m_{oil} \cdot m_c^{-1} = \rho_{oil} \cdot V_{oil} \cdot m_c^{-1}, \text{g/g}
\]  

where: \( m_{oil} \) — the mass of oil (patrol, diesel, oil, kerosene), g; \( \rho_{oil} \) — the density of oil (patrol, diesel, oil, kerosene), g/cm\(^3\); \( V_{oil} \) — volume of oil (oil product), cm\(^3\).

4. Results and discussion
By-products of the woodworking industry (sawdust), agricultural production (straw, chaff) and utilities (tree leaves), which accumulate in large volumes, can be used directly as sorbents to clean the aquatic environment from oil pollution (table 1).

Their absorption-sorption properties and structural characteristics indicate that they are best in sawdust, and the lowest leaves of trees.

When using sorbents of plant origin, to purify water from petroleum products, it should be borne in mind that they would have high sorption-absorption properties and buoyancy, were practical to use. As
for the practicality of their use, the leaves of trees, due to the ease of transfer (demolition in certain places) is difficult in real conditions, including on water, to apply.

Table 1. Structural and sorption characteristics of vegetable raw materials at natural humidity.

| Index          | Sawdust | Straw | Leaf |
|----------------|---------|-------|------|
|                | pine    | walnut| birch|      |
| $a$, g/g       | 2.5     | 2.1   | 1.7  | 1.5   | 1.0  |
| $V_s$ (C$_6$H$_6$), cm$^3$/g | 0.07    | 0.03  | 0.03 | 0.03  | 0.2  |
| $V_s$ (H$_2$O), cm$^3$/g      | 1.0     | 0.05  | 0.04 | 0.04  | 0.04 |
| $A(ESR)$, mg-eq/g             | 2.4     | 1.7   | 1.5  | 0.3   | 0.2  |
| $S_p$, m$^2$/g                | 8.2     | 7.7   | 7.7  | 7.2   | 6.2  |

According to the results of our studies and other researchers, sorbents have a high absorption capacity when the sorption capacity is 2-3 mg-eq/g or more. According to table 1, only pine sawdust meets the following requirements. Sorbents, when cleaning the aquatic environment from petroleum products on the surface, must have good buoyancy, i.e. long and confidently kept on water. I take into account that pine sawdust has the best sorption-absorption properties among sorbents of plant origin, we conducted a study of its oil content at different humidity. The sawdust was dried, with natural and high humidity.

Studies have shown that the carbonization of plant products allows to increase in carbon sorbents, several times, their oil consumption and the amount of sorption in relation to oil and petroleum products in comparison with the raw material (table 2). However, for carbonates from leaves and straw, the sorption capacity does not exceed 0.5 mg-eq/g. The amount of sorption of carbonates from tree sawdust is in the range of 2-3.5 mg-eq/g, but the maximum content of strongly acidic carboxyl groups has a carbonate from pine sawdust.

Table 2. Structural and sorption characteristics of carbon sorbents from vegetable raw materials of different types (optimal carbonization conditions).

| Index          | Sawdust | Straw | Leaf |
|----------------|---------|-------|------|
|                | pine    | walnut| birch|      |
| $a$, g/g       | 11.2    | 5.4   | 4.5  | 4.2   | 2.8  |
| $V_s$ (C$_6$H$_6$), cm$^3$/g | 0.09    | 0.05  | 0.04 | 0.04  | 0.02 |
| $V_s$ (H$_2$O), cm$^3$/g      | 0.12    | 0.09  | 0.07 | 0.07  | 0.04 |
| $A(ESR)$, mg-eq/g             | 3.6     | 2.3   | 2.0  | 0.5   | 0.3  |
| $S_p$, m$^2$/g                | 13.1    | 10.1  | 10   | 10.4  | 6.1  |
| Ash content, %              | 1       | 2.1   | 1    | 21.2  | 15.2 |

During the carbonization of vegetable raw materials, the processes of destruction of polymer chains with the release of volatile simple compounds (carbon monoxide (II), carbon dioxide, hydrocarbons of saturated, unsaturated and aromatic series, ketones, aldehydes, alcohols and organic acids), as well as resinous substances, and mesoporous in the form of craters and cracks, resulting in the development of a porous structure. One of the parameters that affects the oil content of the sorbent is its fractional size (d, mm). The study of carbonates of different fractions obtained under the same heat treatment conditions showed that the best sorption properties are shown by pine carbonate with a fraction size of 0.5 mm, 1 mm, 3 mm, 5 mm, which is graphically shown in figure 1. From the data shown in figure 1 it is seen that the maximum value of oil content of carbon material from pine sawdust fraction 1-3 mm due to the maximum number of paramagnetic centres, as other structural sorption characteristics for all sorbent fractions are approximately the same. Comparison of the sorption capacity of raw materials and carbon sorbents showed that in the process of heat treatment it increases by 3-5 times. Carbonates of sawdust of coniferous trees have 2-2.5 times higher sorption capacity than carbonates of sawdust of deciduous trees. Thus, if in the raw material sawdust of walnut and pine do not differ significantly in oil
content (2.1-2.5 g/g), then in the process of carbonization the sorption capacity of pine sawdust increases 5 times, and walnut – only 3 times.

Taking into account the fact that the sorption of oil and oil products is carried out mainly from the water surface, an important characteristic of the sorbent is buoyancy. When the buoyancy is lost, the sorbent with the absorbed oil product settles to the bottom of the reservoir, contaminating it, contaminating the bottom of the reservoir and possible re-contamination of the water surface in the case of oil desorption. We conducted a study on the buoyancy of carbonates, at different values of temperature and heat treatment time, depending on the duration of their stay on the water surface (figure 2). In this case (figure 2), $M_1$ is the mass of carbonate that remains on the surface of the water, and $M_0$ is its initial mass.

The analysis of the obtained results shows that carbon materials based on pine sawdust, obtained at a temperature of 300 °C for 8-10 minutes, have the best buoyancy – 97-100%. Thus, in the proposed mode of carbonization we obtain hydrophobic sorbents. In our opinion, this can be explained by the fact that in the process of carbonization of cellulose-containing raw materials the last of the components of plant tissues decomposes lignin (active decomposition of lignin occurs in the temperature range 280-325 °C). It is known that the pyrolysis of lignin forms a resin (resin density 0.98 g/cm$^3$), which forms a
A hydrophobic film on the surface of the sorbent. Therefore, in the process of low-temperature one-stage carbonization of plant raw materials, spontaneous hydrophobization of the sorbent surface is carried out.

To confirm the hydrophobic nature of the surface of carbon materials, the wetting heat method was used. From table 3 it is seen that the values of the heat of wetting of carbon material based on pine sawdust correlate with buoyancy data, indicating that the pine carbonate obtained at the optimum heat treatment temperature exhibits the greatest hydrophobic nature.

Table 3. The values of the heat of wetting of carbon raw materials of plant origin.

| Sample name | Conditions of carbonization |  |
|-------------|-----------------------------|---|
|              | The carbonization temperature, $T_c$, °C | Time of carbonization, $\tau_k$, min | Heat of wetting, J/mol |
| Pine sawdust | 450 | 9 | 86.15 |
| Pine sawdust | 350 | 9 | 49.00 |
| Pine sawdust | 250 | 9 | 89.85 |
| Straw         | 300 | 9 | 109.55 |
| Leaf          | 300 | 9 | 89.01 |

Table 4. The absorption time of the oil film by materials of different types.

| Names of materials | Absorption time of oil, minutes |
|--------------------|-------------------------------|
| Technical coal     | 3.3                           |
| Mixture of pine sawdust carbonate: expanded graphite (50:50) | 0.5 |
| Pine sawdust carbonate | 0.7                     |
| Straw carbonate   | 1.0                           |
| Leaf carbonate    | 1.3                           |
| Zeolite            | 1.7                           |

For fast and efficient collection of oil and oil products, the sorbent must have the maximum sorption rate, which will reduce the absorption time of pollutants. As can be seen from table 4, the highest sorption rate is shown by a mixture of pine sawdust carbonate: expanded graphite (50:50) and carbon material based on pine sawdust, which can be explained by the developed porous structure and surface chemistry of the materials.

5. Conclusions

Carbonization of sawdust of trees, straw and chaff of cereals, tree leaves, at a temperature of 200-300 °C for 8-10 minutes, increases the structural-sorption, physic-chemical and absorption characteristics of carbon sorbents.

Carbonized carbon sorbents have a sorption capacity of 3-5 times higher compared to the corresponding indicators of raw materials of plant origin.

Carbon sorbents from sawdust of different species of trees have 1.5-4 times higher sorption characteristics compared to carbonates obtained from straw and tree leaves.

Carbon sorbents from sawdust of coniferous trees have 2-2.5 times higher sorption capacity than carbonates from sawdust of deciduous trees and 4-4.5 times, than carbonates from straw and leaves of trees. In the presence of sawdust of coniferous trees, it should primarily be used as a raw material for carbonization, which will most effectively affect the environmental safety of the environment and environmental infrastructure, at lower economic costs.

References

[1] 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
[2] Melbert A A, Shaposhnikov Y A, Mashensky A V and Voinash S A 2019 Effects of \(8\)\(^{12}/\)12 catalytic converter prestarting on harmful emissions at negative ambient temperatures Journal of Physics 1177 012011 doi 10.1088/1742-6596/1177/1/012011

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

[4] Cruz J F, Matejeova L, Pirilä M, Ainassaaari K, 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 doi 10.1007/s11270-015-2540-1

[5] Morzeta 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 doi 10.1007/978-94-007-3010-6_18

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

[7] 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 1041-1045 doi 10.4028/www.scientific.net/AMR.535-537.1041

[8] Pinchevskia O, Sedliačik J, Horbachova O, Spirochkin A and Rohovskyi I 2019 Properties of hornbeam (Carpinus betulus) wood thermally treated under different conditions. Acta Facultatis Xylologiae Zvolen 61(2) 25-39 doi: 10.17423/afx.2019.61.2.03

[9] 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 Economy, Energy and Environment 1(3) 64-73 doi 10.11648/j.ijeee.20160103.13

[10] 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

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

[12] Rogovskii I L, Titova L L, Trokhaniak V I, Solomka O V, Popyk P S and Shvidia V O, Stepanenko S P 2019 Experimental studies of drying conditions of grain crops with high moisture content in low-pressure environment INMATEH Agricultural Engineering 57(1) 141-6

[13] 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) 1480-90

[14] 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

[15] Haiping Y, Yan R, Chen H and Zheng C 2007 Characteristics of hemicellulose, cellulose and lignin pyrolysis Fuel Journal 86(12-13) 1781-1788 doi 10.1016/j.fuel.2006.12.013

[16] Widner K, Naisse C, Rumpel C and Glaser B 2013 Chemical modification of biomass residues during hydrothermal carbonization Organic Geochemistry 54 91-100 doi 10.1016/j.orggeochem.2012.10.006

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

[18] 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

[19] Klavins M and Porshnov D 2013 Development of a new peat-based oil sorbent using peat pyrolysis Environmental Technology 34(9-12) 1577-1582 doi
10.1080/09593330.2012.758668

[20] Kovalenko O, Novoseltseva V and Kovalenko N 2018 Biosorbents – prospective materials for heavy metal ions extraction from wastewater *Food Science and Technology* **12**(1) 118-22 doi 10.15673/fst.v12i1.841