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Feasibility study of the efficiency of carbon sorbents based on pine sawdust for removing oil products

Abstract. Oil pollution of the environment in many ways stands out among others. It is known, for example, that a litre of oil deprives oxygen of 40 thousand litres of water, and a tonne of oil pollutes 12 km² of the water surface. The content of petroleum products in water above 0.1 mg/l gives fish meat an overwhelming taste and a specific smell of oil during any technological treatments. A wide variety of sorption materials for oil spill response are available on the domestic and global markets. Sorbents are created based on various organic and inorganic materials. Many of them are quite efficient and have a high sorption capacity, but the energy and material costs of their production determine the high cost of the product, which often does not meet consumer requirements. At the same time, promising and cost-effective sorbents can be produced from local secondary raw materials. In recent years, the development of oil sorbents for collecting hydrocarbon leaks based on forest and agricultural industry waste has been actively underway, the use of this type of raw material is conditioned by the rather high absorption capacity of the obtained sorbents, their low cost, availability as a local material, and the possibility of further use. The purpose of the study is to summarise experimental data on the effectiveness of carbon sorbents based on pine sawdust for cleaning petroleum products. The paper presents tabulated data on the structural and sorption characteristics of various fractions of pine sawdust at a humidity of 50-60%. The authors proved experimentally the existence of a dependence of the oil capacity of carbon sorbents from different pine fractions on the duration of carbonation at different temperatures. The paper presents results on the absorption and sorption characteristics of carbon sorbents from different fractions of pine sawdust. Conclusion – at each temperature when carbonation processes were studied, an optimal duration value was obtained at which the oil capacity of the sorbent from different fractions of pine sawdust was the highest, and the yield of the sorbent was maximum. Scientific significance – the authors proved that the carbonation temperature of more than 350°C for pine sawdust of various fractions is not recommended, and for fractions smaller than 1 mm above 300°C, which have a small size and significant burnout and degradation due to the possibility of fire, as a result of which the quantity and quality of carbon sorbent decreases

Keywords: indicators of carbon sorbents, environment, economic indicators, carbonation, petroleum products, sorption capacity, pine fractions

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INTRODUCTION

Petroleum products are a fairly common source of environmental pollution [1]. As indicated in [2], almost 2% of the total amount of fuel and lubricants produced is released into the environment. Both the petroleum products themselves and the impurities they contain are dangerous [3]. In addition, when ingested in soil and water, petroleum products, as a result of physicochemical reactions and

biological interactions, turn into toxic substances that cause harmful effects on biota [4]. Water and soil purification from fuel and lubricants by sorption is organisationally, technologically, economically, and environmentally relevant today [5]. Carbon sorbents based on raw materials of the woodworking industry are particularly important and widespread [6]. The study of the essence of carbonation

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processes, physicochemical, absorbing, and structural sorption properties of carbon sorbents, when the raw material is a by-product of the woodworking industry, namely, pine sawdust, the processes of sorption of petroleum products by them, their environmental and economic substantiation and analysis, requires further study and evaluation.

Petroleum products entering the water and soil environment cause significant environmental changes in them [7]. There is a significant and dangerous pollution of the environment with petroleum products and their decomposition products [8]. Sorbents are effective and widespread means for cleaning soil and aquatic ecosystems [9]. Sorbents are known for their absorption properties in cleaning from various kinds of contaminants [10]. In recent decades, sorbents have become increasingly used in all sectors of the national economy, including for soil and water purification from petroleum products [11]. Carbon sorbents obtained on the basis of by-products of agricultural production [12] and the woodworking industry differ significantly in their properties and characteristics [13]. The technology and processes [14] that occur in the production of carbon sorbents have a significant influence on the sorption parameters of sorbents [15]. Carbon sorbents obtained on the basis of sawdust have better sorption and absorption properties, compared to sorbents obtained from tree leaves and straw [16]. The structure [17], properties [18], ways of obtaining [19], and the use of carbon sorbents based on plant raw materials are investigated [20]. However, the nature, properties, sorption characteristics, physicochemical properties and processes of transformation of by-products of the woodworking industry, namely, sawdust, into carbon sorbents, their complex use for cleaning water and soil ecosystems, environmental and economic assessment, are not thoroughly investigated.

The purpose of the study was to investigate: physicochemical, structural, sorption, and absorption properties of pine sawdust and carbon sorbents obtained from it;

technological processes, technologies, and transformations in the production of carbon sorbents from pine sawdust; the degree and completeness of purification, environmental and economic feasibility, and advantages of using carbon sorbents obtained from pine sawdust in the purification of the aquatic environment and soils from petroleum products.

RESULTS AND DISCUSSION

Pine sawdust accumulated in the woodworking industry has the best physical, chemical, structural, sorption, and absorption characteristics and properties among other sorbents of plant origin. According to the results of our research, sorbents have good efficiency when their absorption capacity of petroleum products is 2-3 g mg-eq/g or more. They can be directly used to clean the soil and water environment in case of contamination with petroleum products. Pine sawdust, at natural humidity, has an absorption capacity of petroleum products in the range of 2.6-2.8 mg-eq/g, which fully meets these requirements, and therefore, it can be used for sorption in case of contamination. The studies (Table 1) show that the physicochemical, structural, absorption, and sorption properties of various fractions of pine sawdust at a humidity of 60% do not significantly differ from each other. The exception is non-sifted sawdust, the absorption capacity of which is slightly lower compared to other fractions, which is conditioned by the presence of small impurities of wood and bark in it, which have low sorption indicators.

When using pine sawdust at a humidity of 60% for cleaning the water or soil environment from petroleum products, it is not advisable to divide it into fractions. It is enough just to install 5-7 mm sieves directly on sawmills, which will separate the smallest particles of wood and bark from sawdust.

However, such sawdust during long-term storage (even when all requirements are met), due to intensive microbiological processes in a humid environment, can quickly deteriorate, and therefore, requires careful and correct storage conditions.

Table 1. Structural and sorption characteristics of various fractions of pine sawdust at humidity 50-60%

Fraction size	a. g/g	SEC. mg-eq/g	Vs (C ₆ H ₆). g/cm ³	Vs (H ₂ O). g/cm ³	S _{pet.} m ² /g
< 1 mm	2.5	2.4	0.07	1.0	8.4
1-3 mm	2.8	2.7	0.07	1.0	8.4
> 3 mm	2.6	2.5	0.07	1.0	8.4
0-5 mm	2.7	2.6	0.07	1.0	8.4
not sifted	2.3	2.2	0.06	0.09	8.0

The structural, physicochemical, absorption and sorption properties of pine sawdust can be improved by the carbonation process.

Carbonation is a method of obtaining carbon sorbents from plant raw materials during heat treatment, which begins when the raw material is heated above 110-120°C. It was established that the carbonation of pine sawdust begins at a temperature of 120-130°C.

Since the hydrocarbon part of pine sawdust consists of cellulose and hemicellulose, and the complex of aromatic compounds – lignin, then during carbonation there are complex processes of destruction of their polymer chains with the

release of both resinous substances of complex structure and a large number of volatile compounds. The carbonation process was studied every 50°C, in the range from 100 to 400°C.

It was established that the process of carbonation of pine sawdust begins at a temperature of 120-130°C. Within the temperature range of 200-300°C, the main decomposition reactions of hemicellulose, cellulose, and lignin take place, resulting in the release of simple carbon compounds (carbon dioxide and carbon monoxide), a liquefied mixture, and resins. At different stages of the carbonation process, the intensity and energy of activation of destructive transformations varies significantly, because at different

temperature ranges, various components of pine sawdust, hemicellulose, then cellulose and lignin decompose. Therefore, the results obtained indicate the complexity of the process of pine sawdust carbonation.

The study of the process of carbonation of pine sawdust fractions allowed establishing that at each studied temperature of the carbonation process, for each fraction, there is a certain optimal value of its duration, at which the oil capacity of carbonate is the maximum, which is graphically shown in Figure 1.

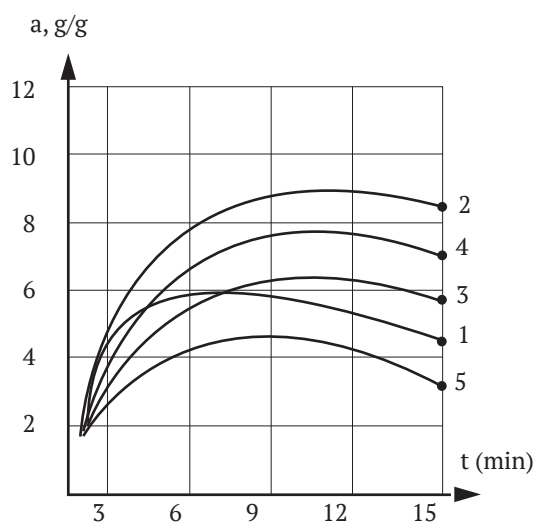


Figure 1. Diagram of links of mobile robot components

The appearance of maxima in Figure 1 is conditioned by changes in the porous structure of sorbents and chemical transformations of the surface of pine sawdust during carbonation. Thus, at the initial stage of the process of carbonation of pine sawdust and its fractions, due to the extraction of moisture, the release of gases, volatile simple substances and resinous compounds, pores are formed, which leads to an improvement in physicochemical and structural parameters, an increase in its sorption capacity of petroleum products to a certain maximum value. This improves the porosity of the carbon material.

According to the studies, the obtained carbon sorbents, due to carbonation of various fractions of pine sawdust, have several times higher oil capacity to petroleum products, better sorption, physicochemical and structural indicators, compared to the initial product (Table 2). Carbon sorbents from sawdust of 1-3 mm fractions have the highest sorption capacity for petroleum products and reach almost 12 g/g. Slightly lower sorption values (almost 10 g/g) for sorbents from sawdust of 0-5 mm fractions. Carbon sorbents made from sawdust fractions larger than 3 mm have a sorption capacity of 8 g/g, while fractions up to 1 mm have a sorption capacity of about 7 g/g. Carbon sorbents made from non-sifted sawdust had the lowest oil capacity, which is conditioned by the presence of small particles of wood and bark in it, which have low sorption properties. After analysing the study results, which characterise carbon sorbents obtained from different fractions of pine sawdust, it can be concluded that sorbents from sawdust fractions of 1-3 mm have the best sorption properties.

However, the oil capacity of the feedstock of sawdust of different fractions did not differ much from each other. The maximum value of the oil capacity of carbon material from pine sawdust of the 1-3 mm fraction is conditioned by the presence of the maximum number of pragmatic centres, since other structural and sorption characteristics for all sorbent fractions are approximately the same.

Special attention should be paid to the analysis of carbon sorbents obtained from different fractions of pine, in matters of their practical use, for cleaning water and soil media from petroleum products (they can be used for cleaning other pollutants). After analysing the sorption, environmental, and economic feasibility and efficiency of carbon sorbents obtained from different fractions of pine, it was concluded that in practical use for cleaning the environment, it is necessary to use carbon sorbents obtained from (without dividing into fractions) sawdust (0-5 mm), from which only wood and bark impurities were separated. That is, sawdust in which all fractions are present (ordinary sawdust). To do this, sawdust on sawmills should be sifted on a sieve of more than 5 mm (up to 10 mm), from which small remnants of wood and bark are removed).

Table 2. Absorption and sorption characteristics of carbon sorbents from various fractions of pine sawdust

Fraction size. mm	a. g/g	SEC. mg-eq/g	Vs(C ₆ H ₆). g/cm ³	Vs(H ₂ O). g/cm ³	S _{pet.} m ² /g	Number of PMCs. spin/g
< 1	6-7	3.4	0.11	0.07	14	10.3·10 ¹⁸
1-3	10-12	3.6	0.12	0.09	13	13.9·10 ¹⁸
> 3	7-8	3.5	0.11	0.08	12	12.8·10 ¹⁸
0-5	9.5-10.5	3.5	0.11	0.08	12	13.1·10 ¹⁸
not sifted	5-6	3.2	0.10	0.06	11	9.2·10 ¹⁸

Carbon sorbents obtained from sawdust (without division into fractions), to a certain extent, are inferior in sorption indicators to carbon material obtained from a sawdust of 1-3 mm fraction. However, these advantages do not compensate for the cost of dividing sawdust into fractions, given that the very separation of raw sawdust into fractions is very difficult due to the clogging of the sieve, which requires additional equipment and technology.

Indicators of sorption capacity of sifted pine sawdust and carbon sorbents presented in Tables 1 and 2 indicate that during heat treatment it increases by almost 1.5, and oil capacity by almost 4 times.

At each temperature of carbonation process, an optimal duration value was obtained at which the oil capacity of the sorbent from different fractions of pine sawdust was the highest, and the yield of the sorbent was maximum. The

carbonation temperature of more than 350°C for pine sawdust of various fractions is not recommended, and for fractions smaller than 1 mm above 300°C, which have a small size and

significant burnout and degradation due to the possibility of fire, as a result of which the quantity and quality of carbon sorbent decreases (Table 3).

Table 3. Weight loss by various fractions of pine sawdust during carbonation

No.	Tk. °C	τ. min.	Weight loss. %
1	250	9.5	55
2	300	9.5	60
3	350	7.0	70
4	400	4.5	75
5	450	4.0	80

The optimal carbonation temperature for all pine sawdust fractions is 300°C with a process duration of 9-9.5 minutes, and for fractions – up to 1 mm 250°C with a duration of 10-10.5 minutes.

CONCLUSIONS

1. Carbonation of pine sawdust should be carried out at a temperature of 200-300°C, for 8-10 minutes, which increases the structural, sorption, and absorption characteristics of carbon sorbents.

2. Carbon sorbents obtained in the process of carbonation of pine sawdust (without admixtures of wood and bark) have a sorption capacity of almost 1.5 times, and oil

capacity is almost 4 times higher compared to the corresponding indicators of the initial product.

3. Carbon sorbents obtained from the 1-3 mm pine sawdust fraction have the best physicochemical, structural, sorption, and absorption characteristics.

4. For cleaning water and soil from petroleum products, it is economically and practically advisable to use carbon sorbents obtained directly from pine sawdust without dividing it into fractions (ordinary sawdust from 0-5 mm from which wood and bark impurities are removed). Such sorbents are somewhat inferior in sorption characteristics to sorbents obtained from pine sawdust of 1-3 mm fractions, but they are much cheaper.

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Техніко-економічне обґрунтування ефективності вуглецевих сорбентів на основі тирси сосни для очищення нафтопродуктів

Анотація. Нафтові забруднення довкілля багато в чому виділяються серед інших. Відомо, наприклад, що літр нафти позбавляє кисню 40 тисяч літрів води, тонна нафти забруднює 12 км² водної поверхні. Вміст у воді нафтопродуктів вище 0,1 мг/л надає м'ясу риб непереборний при жодних технологічних обробках присмак і специфічний запах нафти. На вітчизняному та світовому ринках є велика різноманітність сорбційних матеріалів для ліквідації нафтових розливів. Сорбенти створюються на основі різних органічних та неорганічних матеріалів. Багато з них є досить ефективними і мають високу сорбційну ємність, проте енергетичні та матеріальні витрати на їх виробництво визначають високу вартість продукту, що часто не задовольняє вимог споживачів. Водночас перспективні та економічно вигідні сорбенти є можливим виготовляти з місцевої вторинної сировини. В останні роки активно ведуться розробки з отримання нафтових сорбентів для збору проток вуглеводнів на основі відходів лісової та сільськогосподарської промисловості, використання цього типу сировини обумовлено досить високою поглинаючою здатністю одержуваних сорбентів, їх низькою вартістю, доступністю як місцевого матеріалу та можливістю подальшого застосування. Мета статті – узагальнення експериментальних досліджень з ефективності вуглецевих сорбентів на основі тирси сосни для очищення нафтопродуктів. В статті представлені табульовані дані про структурні та сорбційні характеристики різних фракцій тирси сосни при вологості 50–60 %. Авторами доведено експериментальним шляхом існування залежності величини нафтоємності вуглецевих сорбентів із різних фракцій сосни від тривалості карбонізації при різних температурах. В статті подано результати про поглинальні та сорбційні характеристики вуглецевих сорбентів із різних фракцій тирси сосни. Висновок – при кожній температурі, коли досліджувалися процеси карбонізації, маємо оптимальне значення тривалості, при якому нафтоємність сорбенту з різних фракцій тирси сосни є найвищою, а вихід сорбенту максимальний. Авторами доведено, що температура карбонізації тирси сосни різних фракцій більше 350°C не рекомендується, а для фракції менше 1 мм понад 300°C, яка має малі розміри та значне вигорання і деградацію, через можливість загоряння, внаслідок чого знижується кількість та якість вуглецевого сорбенту

Ключові слова: показники вуглецевих сорбентів, довкілля, економічні показники, карбонізація, нафтопродукти, сорбційна ємність, фракції сосни