Classification of the sorbents capable of removing the petroleum products from Wastewater

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Abstract. Currently, an effective and relatively cheap sorption material for the extraction of various pollutants from water is being actively sought. It is still relevant the use of the sorbents made on a natural basis. Different material modifications, which make it possible to achieve the high values of their sorption capacity, are being studied. The new Classification of the sorbents used in the technologies for treating wastewater from the oil products, in this paper is presented. The all characteristics of the sorbents are considered in the work. An algorithm is formed that allows one to make an informed choice of the sorbent in terms of its effectiveness, environmental protection and material costs. As an example, the pine sawdust characteristics at the Classification is performed. Sawdust can be considered as an effective base of the sorbents, characterized by environmental safety, cheap raw materials and ease of use.

1. Introduction
The petroleum products are one of the most common and dangerous pollution of the surface water bodies. The treating problem all types of wastewater from oil products is relevant for the Tyumen Region that is the leader in the Russian Fuel Industry.

At present, the development of the water purification technologies, which make it possible to the extract the oil products with minimal costs, is very relevant. The most important place in the technological schemes of the treatment facilities is sorption treatment [1-3].

The sorbents characteristics in the paper are considered. An algorithm, that allows one to choose sorbents with maximum efficiency for ecology and economics, is formed. Attention to the issues of the production environmental friendliness and various factors effectiveness is paid.

2. Review
The main source of environmental pollution by oil products is considered untreated or partially treated industrial wastewater from the oil, fuel, metallurgical, transport and other industries. A significant amount of oil products also gets into the water bodies from the adjacent industrial areas during the rainy seasons and active snowmelts [4].

The petroleum products concentration in the rivers of the Tyumen Region exceeds the established values by tens of times. One of the main reasons for the pollution of water resources with oil products is the discharge of untreated industrial and surface wastewater into the water bodies [5, 6].

In water, the petroleum products may be in a free, bound or dissolved state. It is difficult enough to choose the best water cleaning method. The sorption methods are the most optimal, easy to automate
and do not require the large operating costs. Therefore, sorbents analysis can be the starting point in the formation of the optimal solutions in this issue [7].

Almost any sorption process is characterized by capillary catching, adsorption, chemisorption, or absorption. Depending on the binding energy of the sorbate and the sorbent, adsorption can occur due to adhesion (without changing the chemical composition of the sorbate) or to the chemical bonds between the matters.

In recent years, the scientists and specialists interest in the development and use of mineral and synthetic sorbents, as well as sorbents based on the very cheap plant wastes, has increased significantly [3,8].

The sorption material properties depend on the chemical composition and physical state of its surface, porosity and specific surface. The analysis of the structural characteristics and surface properties allows evaluating the effectiveness of the sorption materials use in the water treatment process from the oil products. The right choice of sorbent or a good combination of several sorbents influence to extraction the various compounds in a wide range and to treatment of the large water volumes before the appearance of the oil products in the filtrate [6].

3. Problem
Currently, there is no generally accepted classification of the sorbents used in the technologies for treating wastewater from petroleum products. The scientific literature presents the various sorbents classifications of inorganic or organic nature, from the plant or synthetic materials. Most often, their classification is based on the following characteristics: the nature of wetting with water, structure, purpose, oil sorption capacity and the special properties. Such a generalized approach to the classification of all types of the sorbents does not allow a qualified comparative analysis, does not reveal the main essence of the materials used and does not allow to draw any conclusions on the specific areas of their use [8].

The objective of this science work is the more fully systematize of the sorbents used in wastewater treatment, depending on their main characteristics and parameters, as well as on the economy and environmental friendliness. The analytical materials will help to form an idea of the sorption materials, identify their characteristics and make the right choice of the sorbents.

4. Theoretical part
A.V. Kiselev developed an adsorbents classification with their separation into the structural types, characterized by the nature of the pores volume distribution by size and shape. This classification greatly facilitated the study of the highly dispersed bodies and opened up great the opportunities for a scientific approach in the sorbents selection. The main ones: non-porous, uniformly large-pore, uniformly finely porous and mixed [9]. Based on a large amount of experimental material, this classification was supplemented and refined periodically [10]. According to the Kiselev's classification the sorbents are divided into 3 types [9]: 1) the non-specific sorbents, on the surface of which there are no the functional groups and ions; 2) the sorbents having positive charges on the surface; 3) the sorbents having the bonds on the surface or the groups of the atoms with a concentrated electron density.

According to the IUPAC nomenclature, all porous materials are divided into 3 classes: 1) the microporous materials (a characteristic pore size \( R < 2 \) nm); 2) the mesoporous materials (2 \( < R < 50 \) nm); 3) the microporous materials (\( R > 50 \) nm). The macrospores mainly perform a transport function, and sorption is carried out in the micro- and mesoporous [11,12]. The pores with diameter from 1.5 to 4.5 nm provide the greatest oil recovery effect [13].

The modern sorbent materials must meet such important requirements as the environmental friendliness, low material costs and ease of use. Thus, the classification of the sorbents can be varied and include the nature of its origin and physicochemical characteristics, the sorbents modifying, regenerating and utilizing methods [1,2,14,15,7].
For practical use, the shape of the sorbents, which dispersed (powders, chips, granules) or molded (rolls, mats, booms), is important. The molded synthetic sorbents are easy to use and easy to clean, but they are more difficult to dispose of. The efficiency of the using molded sorbents is low. The dispersed sorbents can be use in any quantity, but are difficult to apply and collect after using [15].

The use of any sorbents implies the presence of auxiliary equipment, and therefore the parameters «According to the method of use» and «By the level of complexity of sorbent extraction» are included in the Classification, offered by this paper.

Some types of the sorbents have the special properties useful for solving the practical problems. For example, the biosorbents contain the immobilized microbiological cultures that decompose petroleum products to the simple compounds much faster than in the natural conditions. The sorbents with the magnetic properties are designed for use in the hard-to-reach places; these sorbents are easily removed from water by the magnetic traps. Some sorbents contain the reagents that are hardeners of oil. This kind of reagents simplifies the contaminant collection from water [15].

The sorbents for eliminating oil pollution, that currently used, are either expensive or require the additional costs for disposal. In fact, the sorption ability of the natural materials is actively studied. All natural materials are capable of absorbing oil and oil products, but have a low sorption capacity. The natural phytosorbents are characterized by high water absorption, which is associated with the presence of the polar groups (OH, COOH and others). These groups create the significant free force fields, and, as a result, reduce the sorbent's effectiveness. The various modifications allow increasing oil sorption capacity [3] and reducing water absorption of sorbents [16]. In this regard, the “Surface condition” and "The modification method" parameters have been added to the new Classification.

From the point of view of environmental safety, some authors [17] proposed the parameter “The disposal degree”, which divides the sorbents into three groups: 1) unutilized; 2) partially recyclable; 3) recyclable.

There is a problem of spent sorbents disposal with absorbed sorbate. Most often, the spent sorbents are burned, therefore often leads to secondary environmental pollution. Some regeneration methods allow the extraction of the absorbed substances from the spent sorbents. From the point of view of environmental safety and economics, the new Classification proposed features: “The use degree”, “The environmental friendliness degree of the spent sorbent disposal”, “The regeneration method” and “The extraction degree of the sorbate”.

5. Results
Based on the existing classifications and comparisons of petroleum sorbents [1,2, 9-11,7,17,13], and also taking into account the proposed additions, the author of this article proposes a generalized systematization of sorbents used in the wastewater treatment technologies (table 1).

Due to environmental cleanliness, a wide raw material base and oil intensity at a relatively low cost, the sorbents based on waste from the forest and agricultural industries can successfully compete with the industrially produced analogues [18]. When studying the pine sawdust properties at the Department of Water Supply and Sanitation of Tyumen Industrial University, a modification to change the sawdust structure under the chemical (ozone treatment) and physical (SHF) effects, has done [19, 20].

Based on the research, as well as the works of other authors [3,7,13,18,21], the sawdust description is compiled in accordance with the full Classification proposed above:
1. By basis type: organic – natural – of plant origin (phytosorbents) and waste from their processing;
2. according to the use method: loaded into filters to remove bulk water contaminants;
3. in shape: dispersed – coarse (more than 50 microns);
4. by porous structure: heteroporous (the radius of pores curvature varies over a wide range);
5. by the nature of wetting: hydrophilic (static angle of sorbent material wetting with water is less than 90°);
6. by buoyancy: non-floating (up to 3 hours);
7. by water absorption: average (1-10 g/g);
8. by oil sorption capacity: low (less than 5 g/g);
9. by absorption rate: high (less than 10 minutes);
10. by use degree: single use;
11. by the level of sorbent extraction complexity: 2 – ease of extraction;
12. by surface condition: modified;
13. according to the modification method: restructuring – chemical exposure and physical impact;
14. by degree of disposal: partially recyclable;
15. by the environmental friendliness degree of the spent sorbent disposal: 2 – burning;
16. by the regeneration method: not subject;
17. according to the extraction degree of the sorbate: non extracted.

Table 1. Classification of the Sorbents capable of removing the Petroleum Products from Wastewater.

| The Classification parameters of the sorbents for wastewater treatment from petroleum products |
|---|
| **Basis type:** |
| inorganic from natural minerals | from artificial inorganic materials |
| organic natural | synthetic from caustobioliths of plant origin (phytosorbents) and waste from their processing animal origin and waste from their processing |
| **The use method:** |
| applied to the surface to remove surface water contaminants | loaded into filters to remove bulk water contaminants mixed and defended |
| **The shape:** |
| finely divided (less than 50 microns) (powders) | dispersed | coarse (more than 50 microns) (crumbs, granules, flakes) |
| molded | fibrous (woven and non-woven materials) | pressed (plates or products of a different configuration) | combined (sorbing booms, pillows, mats with a shell of permeable material) |
| **Porous structure:** |
| non-porous large pore (pore curvature radius of more than 200 nm) mesoporous (radius of curvature of pores 1.5-200 nm) finely porous (pore curvature radius less than 1.5 nm) heteroporous (the radius of curvature of the pores varies over a wide range) with isotropic porosity with anisotropic porosity |
| **Wetting nature:** |
| hydrophilic (static angle of wetting of the sorbent material with water is less than 90 °) indifferent wetting (the static contact angle of the sorbent material with water is approximately 90 °) hydrophobic (the static contact angle of the sorbent material with water is greater than 90 °) |
| **Buoyancy:** |
| high buoyancy (more than 72 hours) | limited buoyancy (3 - 72 hours) | non-floating (up to 3 hours) |
| low (less than 1 g / g) average (1-10 g / g) high (more than 10 g / g) |
| **Water absorption:** |
| low (less than 5 g / g) average (5-15 g / g) high (more than 15 g / g) |
| **Oil sorption capacity:** |
| low | average | high |
| less than 10 minutes 10-30 minutes more than 30 minutes |
The special properties:

| magnetic (with the addition of magnetite) | swellable | containing surfactants - oil dispersants | containing reagents - oil thickeners | containing bacterial cultures for biodegradation of hydrocarbons | other (variable density, ion exchange, etc.) |
|------------------------------------------|-----------|------------------------------------------|-------------------------------------|---------------------------------------------------------------|-----------------------------------------------|
| with core-shell structure                | with core-inorganic shell structure |                                          |                                     |                                                               |                                               |

The use degree:

| single use | reusable |
|------------|----------|
| no extraction required | ease of extraction |
| extraction difficulty |

Complexity level of sorbent extraction:

1. no extraction required
2. ease of extraction
3. extraction difficulty

Surface condition:

| non changed | activated | modified |
|-------------|-----------|----------|

The modification method:

| surface change | curing | hydrophobization |
|----------------|--------|------------------|

| increase in surface area: | restructuring | physical impact |
|---------------------------|---------------|------------------|
| - heat treatment; | | electromagnetic radiation: |
| - mechanical restoration; | | - infrared radiation; |
| - chemical treatment | | - microwave radiation; |

The disposal degree:

| unutilized | partially recyclable | recyclable |
|------------|----------------------|------------|

The environmental friendliness degree of the spent sorbent disposal:

1. spin-burial
2. burial firing
3. burial burning
4. use as a recyclable materials
5. biodegradation
6. landfill for natural decomposition (under the influence of several natural factors)

The regeneration method:

| destructive | regenerative |
|-------------|--------------|

| chemical treatment with organic and inorganic reagents | low temperature (thermal) (at a temperature of +100 °C more than +100 °C) | thermal treatment (at a temperature of +350 °C to +600 °C) |
|------------------------------------------------------|--------------------------------------------------------|----------------------------------------------------------|
| recovery of absorbed matter; | - thermal distillation of the sorbate by water vapor; | - organic solvent extraction; |
| - thermal distillation of the sorbate by water vapor; | - dissociation of a weak electrolyte in an equilibrium solution; | - sorbate evaporation under the influence of an inert gaseous coolant flow. |
| spin burning out | | spin burning out |

The extraction degree of the sorbate:

| non extracted | low (less than 30%) | average (30-60%) | high (over 60%) |
|---------------|---------------------|------------------|-----------------|

6. Conclusion

The developed Classification includes the various parameters of the sorbents capable of extracting oil products from wastewater, depending on their most significant characteristics and technological parameters. The classification gives a more complete picture of both the sorbents themselves and the methods for their preparation, processing, use and disposal. This will make a reasonable choice of the sorbents in terms of application efficiency, environmental protection and material costs. The studies and the Classification based on them, showed that pine sawdust should be considered as an effective sorbent based, characterized by environmental safety, cheap raw material base and ease of use.

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