Process Intensification of the Petroleum Product Extraction from the Aqueous Solutions by Natural Sorbents

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Abstract. Nowadays, an effective and relatively cheap sorption material for the various pollutants’ extraction from the water is being actively sought. It is still relevant to use the naturally made sorbents. Different material modifications, which make it possible to achieve the high values of their sorption capacity, are being studied. The waste products which can be used in the wastewater treatment technology as the secondary raw materials are of the greatest interest. In this scientific work, the activated carbon and the pine sawdust have been used as the sorbents. The effect of the microwave radiation (SHF) and ozonization on the sorption process of the oil products from the aqueous solutions by affecting both the sorbent and the solution has been studied. The regression equations describing the sorption processes depending on the heating temperature, time and methods of treatment, have been obtained.

1. Introduction
The pollution of water resources is a serious environmental problem of our time. The rapid development of industry, agriculture and human living conditions has led to a deterioration of the surface water and groundwater quality around the world [1]. The total number of the water bodies suitable for drinking needs has globally decreased [2].

The oil products are one of the most common and dangerous pollutants of the water bodies. The wastewater which contains the petroleum products is formed at the oil producing, oil refining, metallurgical and chemical industry enterprises. A huge quantity of oil products enters the water bodies with a land runoff which is characterized by a high concentration of season contaminants.

One of the most effective, environmentally safe and cost-effective methods of the wastewater treatment is sorption. With this method, the purification effect is able to reach 99% [3].

2. Review
When choosing a sorption material, much attention is paid to its sorption characteristics, as well as to the manufacturing cost and the availability of raw materials [3, 4].

The sorbents which are based on the inorganic materials (diatomite, zeolites, clay, sand) have a low oil sorption capacity. They have hydrophilic properties, require additional modification, cause the difficulties with the utilization and completely do not retain the light fractions of the petroleum products. The synthetic sorbents have a good absorption capacity, but they are characterized by higher cost and disposal complexity due to the high toxicity of the combustion products. The most promising direction is the improvement of the natural sorbent production technology on the basis of the plant residues and production waste.
Currently, an active search for the material, that allows the most effective control of oil pollution sorption and has a relatively low price, is being made.

According to popular opinion, the activated carbon remains the most used and the most effective sorbent. The useful effect of the activated carbon is able to reach 99%. The disadvantages of using this sorbent are its cost, expensive regeneration and the limited life. Traditionally, both active carbon itself and other sorbents based on it, for example, "Busofit", are used as loading of oil-collecting filters. [5].

The known sorbent "Ecolan" has been made on the basis of the activated carbon, mineral components and an oil-oxidizing bacteria strain. As the producers say, it is one of the effective biosorbents. The "Ecolan" refers to the class of the biodegradable sorbents, which localize the oil pollutants and destroy the adsorbed petroleum products by a biological method. The material has an efficiency of more than 94% and operates over a wide temperature range from +5 to + 40 ° C. [6].

The filters with the polyurethane foam loading (or "PUF-loading"), which are the effective and economical means for the deep effective treatment from the emulsified and colloidal impurities, can be the alternative variant. The sheet or lump of PPU material (in the form of cubes with size 25-40 mm), and even the waste of this material in the form of scraps can be used as a filter load. According to the manufacturers, the PPU-loading increases the degree of purification from oil products to 99.8%. For the regeneration of the filter material, the "PUF-loading" mechanical wringing out is usually sufficient. The filter washing water consumption, as compared to the conventional filter materials, is reduced from 2% to 0.05-0.2% of the filtered water volume. [7].

Russian LLC company "Rospelimer" has offered the sorbent "NES" which is based on the natural aluminosilicate (vermiculite) and hydrophobized by special technology. It is used for the oil product spill liquidation; its flotation capacity is more than 95%. It has a high buoyancy on the water surfaces. In addition, it is absolutely harmless to the environment: it does not introduce secondary pollutants and does not disturb the ecological balance in case of the continuance on the water. Also, this company has presented the sorbent "UniSorb", which is made on the basis of the expanded polymer under a special temperature regime. The degree of the water purification from the oil products with the use of "UniSorb" is able to reach 98-99.5% [8].

In recent years, in Russia and abroad, the industrial waste recycling has been introduced actively [9]. In the process of the forest and agricultural enterprises' work, the wood shavings and sawdust, the plant waste are formed in quantities. At present, the sorption capacity of these wastes has been intensively studied. In many scientific researches it has been established that the husks, pericarp, the agricultural crop straw, the lignin, the wood sawdust and shavings possess a quite good oil products sorption capacity. The wood industry waste has a more porous structure, it is less buoyancy and more hydrophilic. The petroleum product sorption occurs both on the surface and inside the material pores. On the contrary, the plant waste is more hydrophobic, its structure is less porous. More likely, the sorption occurs on the surface [10-13, 14, 15].

In the process of studying the sorption properties of several natural sorbents and industrial waste, it has been determined that the oil product sorption capacity of the sawdust is 1.5 times higher than the sorption capacity of the lignin, peat and expanded clay [14]. The sawdust is a large-tonnage waste of the timber industry, and this makes it a cheap secondary material. The utilization of sawdust as an oil product sorbent is very promising [15].

The sawdust absorbs the oil and petroleum products and moisture quickly. To increase their sorption activity, it is necessary to provide the additional modification of their surface. One of the methods to hydrophobize the sawdust surface is to treat this material with the water-repellent compounds, for example, fatty acids [16]. Also the effectiveness of the natural sorbents is affected by the functional groups on the surface of the sorbent, the porosity and the surface morphology. The sorbent surface modification with the help of the acids, alkalis, heat treatment in a drying cabinet at various temperatures has been suggested by the authors [17]. For example, according to the results of the experimental work [18], it was established that the best values of the water and oil products absorption have been obtained for the sorbent samples treated with a 3% solution of nitric acid.
3. Problem

The main problem associated with the use of natural materials as the sorbents is the insufficiently significant sorption properties of the plant materials. The solution of this problem is in the modification of such material, i.e. the improvement of its sorption properties and, consequently, the effectiveness of its use [9-15].

The traditional methods of the sorbent modification are: 1) the treatment with the solutions of salts, alkalis or acids; 2) the hot steam treatment. The physical and physicochemical methods of sorption material stimulation, such as the electromagnetic microwave radiation and ozonization (ozone treatment), are less traditional sorbent treatment. For these unusual methods of the sorbent modification, it is necessary to set the parameters of processing regimes. The problem of preliminary physical and physicochemical effects on solutions, which contribute to a process of sorption further, has also been poorly studied.

The purpose of this experimental work is to determine the intensification degree of the sorption processes of petroleum products using various physicochemical methods of the sorbent modification and preliminary preparation of aqueous solutions. It is necessary to increase the sorption filter efficiency and, consequently, to reduce the material costs for the wastewater post-treatment. To solve the problem several experimental tasks have been offered:
- to investigate the effect of the microwave radiation and ozonization on the processes of the petroleum product extracting from the aqueous solutions;
- to consider the various combinations of the external physicochemical effects on the sorbents and aqueous solutions.

4. Description of studies

The article presents the sorbent (the activated carbon and the pine sawdust) and the sorbate (the water-soluble petroleum products in model solution) as the research objects. Activated coconut coal NWC 12x40 is a granule with a size of 0.4-1.7 mm, with a bulk density of 0.48 g/cm³ and a specific gravity of 1.65 g/cm³.

The pine sawdust is obtained as the waste in the process of cutting sawn timber in the carpentry workshop of one of the Tyumen enterprises. The sawdust particle sizes are of 1-5 mm. The following characteristics of the investigated sawdust have been determined: the bulk density is 0.185 g/cm³, the bulk volume is 5.405 cm³/g, the density is 2.181 g/cm³, the true specific volume is 0.459 cm³/g, the volume of the intergranular space is 4.946 cm³/g.

The oil lubricant for Mobil Rarus SHC 1025 air compressors (made in France), having the following physicochemical characteristics: the kinematic viscosity at +40 °C is 44 cSt, at +100 °C is 7.2 cSt; the pour point is -39 °C, the flash point is +246 °C, the specific gravity at +15 °C is 0.849 g/cm³, has been used as a sorbate.

The sorption process has been modeled in the aqueous solutions of the petroleum products prepared on the oil basis, with different concentrations: 35; 23; 16; 10; 5; 1.3; 0.55 mg/l. The oil product concentrations in the working solutions have been fixed for 24 hours, 48 hours and 72 hours using the Fluorat 02-3M instrument [19-23].

To study the effect of various sorbent modifications and to prepare the working solutions for the sorption of petroleum products, several options have been proposed: a) the ozone treatment of the sorbent for 2 and 5 minutes; b) the microwave treatment of the sorbent for 5 minutes; c) the solution preheating with the microwave radiation to a temperature of +40 and +60 °C, followed by the addition of the sorbent; d) the preheating of a mixture (solution plus sorbent) with the microwave radiation to a temperature of +40 and +60 °C; d) the pre-treatment of the solution with ozone for 2 minutes. In all cases, the sorption process has been modeled in static conditions.

For each type of impact, a correlation field was constructed. All correlation coefficients are in the range of 0.95-1, and the correspondence of the regression lines to the experimental data is high. Several regression equations and maximum sorption capacity are shown in the Table:
Table 1. Regression equations and maximum sorption capacity.

| Treatment                                                                 | Activated carbon                  | Pine sawdust                      |
|---------------------------------------------------------------------------|-----------------------------------|-----------------------------------|
|                                                                           | Regression equations               | Maximum sorption capacity, mg/g    | Regression equations               | Maximum sorption capacity, mg/g    |
|                                                                           | y = 0.0199x                        | 0.695                             | y = -0.00001x^3 + 0.00078x^2 + 0.00097x – 0.0044 | 0.56 |
| 1. Model solutions without treatment                                     |                                   |                                   | y = 0.00003x^3 – 0.0013x + 0.004          | 0.58 |
| 2. The solution preheating with microwave radiation to a temperature of +40°C | y = 0.0195x                        | 0.682                             | 0.0002x^3 + 0.0042x^2 – 0.013x + 0.004   | 0.58 |

Maximum solution concentration is 35 mg/l

|                                                                           |                                   |                                   | y = 0.00001x^3 + 0.00078x^2 + 0.00097x – 0.0044 | 0.009 |
|                                                                           |                                   |                                   | y = 0.00003x^3 – 0.0013x + 0.004          | 0.013/|
|                                                                           |                                   |                                   | y = 0.00003x^3 – 0.0013x + 0.004          | 0.014 |
|                                                                           |                                   |                                   | y = 0.00003x^3 – 0.0013x + 0.004          | 0.021 |
|                                                                           |                                   |                                   | y = -0.00002x^3 + 0.001x^2 + 0.0017x + 0.0008 | 0.034 |

Maximum solution concentration is 5 mg/l

|                                                                           |                                   |                                   | y = 0.00001x^3 + 0.00078x^2 + 0.00097x – 0.0044 | 0.009 |
|                                                                           |                                   |                                   | y = 0.00003x^3 – 0.0013x + 0.004          | 0.013/|
|                                                                           |                                   |                                   | y = 0.00003x^3 – 0.0013x + 0.004          | 0.014 |
|                                                                           |                                   |                                   | y = 0.00003x^3 – 0.0013x + 0.004          | 0.021 |
|                                                                           |                                   |                                   | y = -0.00002x^3 + 0.001x^2 + 0.0017x + 0.0008 | 0.034 |

Based on the obtained data, the sorption isotherms have been constructed. According to the Brunauer, Emmett, Teller (BET) classification [20], the sorption isotherms of the petroleum products on the activated carbon during the modification and solution preliminary preparation refer to first (I) and the second (II) types, which are typical for the microporous sorbents. The sorption isotherms of petroleum products in modified sawdust belong to the first (I) and the third (III) types of isotherms according to the BET classification [20]. These isotherms describe the polynuclear adsorption and strong intermolecular interaction in the sorbate material. In the process of the working solutions’ preliminary preparing by heating with the microwave radiation, the sorption isotherms of the sawdust are the first (I), the fourth (IV) and the fifth (V) types according to the BET classification [20].

Figure 1. Sorption isotherms for model solution with 5-35 mg/l oil product concentrations.
5. Conclusion

The sorption capacity of the activated carbon is high enough, various additional modifications and preliminary preparation of the solutions change the sorption capacity for petroleum products insignificantly (only by 5-10%).

The sorption capacity of the sawdust at high concentrations (35 mg / l) is lower than the sorption capacity of the activated carbon by only 18-20%; at concentrations up to 5 mg / l, the activity of the unmodified sawdust is significantly lower than the activated carbon activity.

Of all the proposed modification methods and preliminary solution treatment for the model solutions with a petroleum product concentration of 35 mg / l, a good result has been obtained when the pine sawdust has been heated with microwave to a temperature of + 40 ° C. In this case, the sorption capacity of the sawdust has been increased by 10%.

Different methods of the sorbent modification have increased the sorption activity of the sawdust in solutions with the initial low petroleum product concentrations (up to 5 mg / l): with the preliminary sawdust ozone treatment – in 1.5 times at an average; with the microwave heating - in 2.3-2.5 times. The preliminary solution preparation (the microwave heating of the solution with low pollutant concentrations) has also increased the sorption capacity of sawdust in 1.5 times.

The best indicators for the low concentration solutions have been obtained by the combined microwave treatment of the solutions and the sawdust at a temperature of + 40 ° C. During this process the sorption capacity of the sorbent has been 3.7-4 times higher than for the sawdust without any treatment.

6. References

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