Investigation of the efficiency of oil-containing wastewater sorption treatment with sawdust and probiotic agent addition

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Abstract: Purification of wastewater from petroleum products is an urgent problem for the Tyumen province as an oil and gas region. The use of natural materials is actively studied in the technologies of sorption cleaning which is the main method for oil pollution removal. One of these new technologies is the wastewater treatment method with the use of probiotic agents. The purpose of this research is to study the effect of probiotics on the degree of dissolved petroleum products extraction from aqueous solutions by phytosorbent (pine sawdust). The photometric method of liquid analysis was used as a standard method of research. As a result of the sorption process study, it was found that the concentration of petroleum products decreased faster and to a minimum value (by 48.68%) when filtering samples through a layer of sawdust soaked in a probiotic solution, which is 2 times more effective than pure sawdust. The sorbent used is environmentally friendly.

1 Introduction

The most significant natural resources of the Tyumen region are oil and timber. The oil and gas industry is one of the most important segments of the regional economy and the main source of pollution. The fuel industry accounts for 86.4% of the regional industrial output. A significant part of oil (64%) and gas (91%)in Russia is extracted in Khanty-Mansi Autonomous District in Ugra and Yamalo-Nenets Autonomous District. Approximately 200-300 million tons of oil and gas condensate and more than 500-600 billion meters of natural gas are produced annually [1]. At the same time, the fuel industry is the main source of environmental pollution with its oil and petroleum products. Besides, the timber industry is also one of the promising sectors of the Tyumen region’s economy. The area of forest plots on the forest fund’s lands amounts to 11,396 million hectares. The value of the manufactured products exceeds 4.96 billion rubles according to the data of the timber industry complex enterprises (Tyumen region). Despite the development, the timber industry has been found to be inefficient in waste management: only 15% of total wood residues resulting from processing are recycled [2].

2 Review

The general state of water bodies of the Tyumen region is unsatisfactory, especially in industrialized areas [1]. Characteristic contaminating components are highly and easily oxidized organic substances, compounds of iron, copper, zinc, manganese, and oil products. One of the main causes of water resource pollution with regional petroleum products is the discharge of insufficiently treated and untreated production and surface (rain and melt) wastewater into water bodies [3].

Petroleum products are among the most harmful chemical pollutants: 1 kg of oil and petroleum products deprives 40 m3 of water of oxygen; 1 ton of oil and petroleum products contaminate 12 km2 of water surface. At a0.2-0.4 mg/dm3concentration of petroleum products, the water receives an oil odor that cannot beremoved by any filtration and chlorination [4]. Insufficiently Treated oil-containing effluents form an oil film on the surface of water reservoirs. Spreading over the water surface, the light fractions of the oil evaporate and dissolve partially and the heavy ones descend into the water column, settle to the bottom and form the bottom contamination. Water pollution with petroleum products significantly impairs animal and plant habitat.The use of such water for cultural and domestic purposes is becoming more difficult.

At present, the removal of petroleum products from water is a rather pressing problem, which is solved by the search for efficient and inexpensive sorption materials. For example, wastes from sawdust processing plants are a form of phytosorbents capable of absorbing oils, fuel residues, and dissolved and undissolved petroleum products. In Russia, wood processing waste belongs to the class V hazards, which has a low impact on the environment.

The strategic direction in waste management is to reduce the amount of generated waste and maximize its use as secondary material resource. Today, waste reduction is also closely related to sustainable economic development in the face of ever-increasing demand for raw materialswith a simultaneous reduction in available reserves and the ultimatedepletionof natural resources. Rational use and reproduction of natural resources and environmental protection guarantee long-term social and economic development and form the basis for the development of future generations. There is an increasing global interest in environmental protection and sustainable development of countries and regions. This is due to global environmental disruption and environmental degradation [5].

Production wastes, which can be used in various processes as secondary raw materials, cause the greatest interest. One of the linesof industrial wastesreuse is their recycling and production of new materials used in various wastewater treatment technologies. In this case, two tasks are solved: enterprisewastewater treatment and waste recycling.

One of the ways of reducing the content of petroleum products, especially phenols, was suggested by Russian scientists [6]. It includes catalytic oxidation of wastewater contaminants with manganese-containing reagents (ferromanganese concretions) in a reactor at temperature 303-343˚K and 5 to 6 pH value. The molar ratio of iron oxide to manganeseions is 1:2; the ratio of the liquid phase to hard-phase mass of concretions is 50-55 l to 1 kg. After oxidation, the effectiveness of phenols reduction is more than 99%.

Currently, an active search is underway for a material that allowsthe most efficient control of the sorption of oil pollutionand has a relatively low price. According to popular opinion, activated carbon remains the most used and the most effective sorbent. The useful effect of the activated carbon can reach 99%. The disadvantages of using this sorbent are its cost, expensive regeneration, and limited service life. In addition, in Russia there are no raw materials for its production (Info main), thus the development of analog sorbents is profitable.

Many authors consider the use of natural-based sorbents promising [7-9]. Various modifications of materials, including production wastes, are studied, which allowsto increase their sorption capacity.When choosing a sorption material, much attention is paid to its sorption characteristics,methods forwaste material recovery and recycling,aswellasto the cost of production and the availability of raw materials [7].

In forestry and agricultural enterprises, wood shavings, sawdust and plant wastes aregenerated in large quantities. Currently, the sorption capacity of these wastes is being intensively studied. The wood industry waste has a more porous structure: it is less buoyant and more hydrophilic. Sorption of petroleumproducts occurs both on the surface and inside the pores of the material. In the process of studying the sorption properties of several natural sorbents and industrial waste, it has been determined thatthe sorption capacity of sawdust of petroleum productsis 1.5 times higher than the sorption capacity of lignin, peat and expanded clay [10]. Sawdust is a large-tonnage waste from the forest industry, which makes it a cheap secondary material. The use of sawdust as a sorbent for petroleum products is promising.

One of the modern wastewater treatment methods is based on the use of probiotic preparations with a large content of the probiotic microorganisms and enzymes intended for the rapid destruction of organic substances in wastewater, which makes it possible to significantly accelerate the process of their decomposition and significantly reduce the usual anaerobic processes, accompanied by the unpleasant odors and the releaseof toxic gases.Probiotic agents (probiotics) are composed of probiotic bacteria and enzymes and do not contain chemical or mineral impurities. Probiotic bacteria are non-pathogenic, non-toxic, have a high adhesive and antagonistic ability to pathogenic and opportunistic bacteria. Probiotic agents are widely used in medicine for disinfection of premises [11,12], in cosmetology, in food industry; they are also used as detergents. Most probiotics include facultative anaerobic bacteria (such as Bifidobacterium and Lactobacillus) and spore-forming aerobic bacteria (Bacillussubtilis, Bacillussubtilisvar. Bacillusamyloliquefaciens, Bacilluslicheniformis, Bacilluspumilus, Bacillusmegaterium, etc.) that contribute to water purification processes [13]. Bacillus bacteria producealargespectrumof enzymes that help break down high molecular weight and hard-to-break organic substances[14].

At the laboratory of the Department of Water Supply and Sanitation (Industrial University of Tyumen, Russia),research is being carried out on thepurification ofwastewater from petroleum products with such a phytossorbentaspine sawdust. The influence of probiotic agents on the efficiency of cleaning from various contaminants is also taken into account.

The purpose of this study is to determine the effect of the complex sorbent “pine sawdust - probiotics” on the degree of purification of aqueous solution from dissolved petroleum products.

3 Materials and methods

The article presents the sorbent (the pine sawdust) and the sorbate (the water-soluble petroleum products in a model solution) as objects of research.

The pine sawdust is obtained as waste in the process of sawing wood in a carpentry shop of one of the Tyumen enterprises. The sawdust particle sizes are 1-5 mm. The following characteristics of the investigated sawdust were determined: bulk density 0.185 g/cm^3, bulk volume 5.405 cm^3/g, density 2.181 g/cm^3, true specific volume 0.459 cm^3/g, intercrystalline spacevolume 4.946 cm^3/g, water absorption5.844 g/g.

Oil lubricant for Mobil Rarus SHC 1025 air compressors (made in France)with the following physical and chemical characteristics: kinematic viscosity at +40 ° C 44 cSt, at + 100 ° C is 7.2 cSt; pour point -39 ° C, flash point +246 ° C, the specific gravity at +15 ° C is 0.849 g/cm^3, was usedto prepare a model solution.

The "Pip Plus Water" probiotic (Chrisal Company,Belgium)was used for the experiment. This preparation is a liquid that contains a large amount (6.36 million/cm^3) of Vacillus bacteria in a sporous state: Bacillus subtilis, Bacillus subtilis var. amyloliquefaciens, Bacillus licheniformis, Bacillus pumilus, Bacillus megaterium, and enzymes.

The sorption process was carried out in static and dynamic modes with various methods of processing the sorbent and samplesof aqueous solution of petroleum products.

The content of petroleum products in the samples was determined by the photometric method. A water sample, in which it was necessary to determine the content of petroleum products, was transferred into aseparating funnel with a capacity of 250 cm^3. 10 cm^3 of hexane was pipetted and rinsed with the vessel containing the sample and placed into a separating funnel. The mixture was stirred for 1-3 minutes, settled until a clear upper layer appears, then separated and transferred to a cuvette where the concentration of petroleum products in the extract was measured using the Fluorat-02-3Minstrument. The aqueous phase was collected in a measuring cylinder with a capacity of 100 - 200 cm^3 and its volume was accurately registered.

Theresearch of sorption purification in static mode was carried out in three versions:

1) Sorption of petroleum products on sawdust - 5 g of sawdust were placed in a glass beaker, 100 cm^3 of a 5 mg/dm^3 model petroleum product solution was poured into it and intensively stirred. After a certain time (24, 48, 72 hours), the concentration of purified water petroleum products was determined.

2) Sorption of petroleum products on sawdust impregnated with a probiotic solution with added sugar. A probiotic solution was prepared in advance: 1 drop of substance per 1000 cm^3 of distilled water with sugar. Then the sawdust was soaked in the probiotic solution for 30 minutes. 5 g of soaked sawdust was placed into a glass beaker, 100 cm^3 of a 5 mg/dm^3 model petroleum product solution was poured into it and intensively stirred. After a certain time (24, 48, 72 hours), the concentration of purified water petroleum products was determined.

3) Sorption of petroleum productsunder the influence of probiotic. A probiotic solutionwas prepared in advance: 1 drop of substance per 1000 cm^3 of distilled water. 100 cm^3 of a 5 mg/dm^3 model oil product solution was poured into a glass beaker, 1 drop of probiotic solution was added andintensively stirred. After a certain time (24, 48, 72 hours), the concentration of purified water petroleum products was determined.

In the case of a single injection of a sorbent in a certain amount per certain volume of treated water, the static sorption capacity (SSC),mg/g, is determined by formula (1) [15]:

$$SSC = \frac{(C_{initial} - C_{final}) \cdot V}{g} \qquad (1)$$

where g = weight of dry sorbent, g; V I = volume of solution poured to sorbent, dm3; $C_{initial}$ = initial concentration of petroleum products in initial water, mg/dm^3; C_{final} = final concentration of petroleum products in purified water, mg/dm^3.

Structures in which the sorption process proceeds in a dynamic mode: the absorption capacity of sorbents is determined not only by the equilibrium capacity, but also by the possibility of using most of it in short-time contact of the liquid with the sorbent. In this regard, the sorption was studiedin a dynamic modeunder laboratory conditions, andsamples of aqueous solutionof petroleum products were processed according to two options:

1) Filtration through a layer of sawdust (5 g) at a constant flow rate of 2-3 dm^3/min.

2) Filtration through a layer of sawdust (5 g) soaked in a probiotic (0.01 mg/dm^3) for 30 minutes at a constant flow rate of 2-3 dm^3/min.

Samples of the aqueous solution were filtered from top to bottom through a column filled with sorbent. The sorbate was transferred from output phase to the sorbent phase. After a certain time, the sorbent is saturated and the petroleum products can no longer be absorbed by the pores of the sorbent. The concentration of petroleum products in the filtrate increases.

The first 50 cm^3 samples of filtrate were drained, and the concentration of petroleum products was measured in the next 100 cm^3 and 150 cm^3. On the basis of the obtained data, values of dynamic sorption capacity (DSC), mg/g, were calculated by formula (2):

$$DSC = \frac{V_r \cdot C_{final}}{m} \qquad (2)$$

whereV_r = volume of solution removed from the column from the start of the experiment till the advent of dissolved substance, dm^3; C_{final} = finalconcentrationofpetroleumproductsinpurifiedwater, mg/dm^3; m = weight of sorbent, g.

The dynamic sorption capacity determines the capacity of the sorbent before thesolutes enterthe filtrate. The full dynamic sorption capacity is also calculated (FDSC).The total dynamic sorption capacity is a potentially possible capacity that corresponds to the state of maximum saturation of all exchanged primary ionic groups of the sorbent.

4 Results

The results of the study of thesorption purificationof an aqueous solution in a static mode are presented in Table 1, which shows that the most pronounced effect is given by a complex sorbent consisting of sawdust impregnated with a probiotic solution.

Table 1. Results of the study of sorption purification of aqueous solutions in a static mode.

Sorbent	Concentrationof petroleum products		Degree of extraction of petroleum products from water E, %	Static sorption capacity (SSC), mg/g
	initial	final(72hours)	72 hours	72 hours
Sawdust	5	4,27	14,6	0,0146
Sawdust soaked in probiotic solution +sugar	5	3,1	38	0,038
Probioticsolution	5	3,81	23,8	0,0238

The obtained sorption isotherms (Fig. 1) show that the maximum static capacity (0.038 mg/g) was achieved upon preliminary soaking of pine sawdust in a probiotic solution:

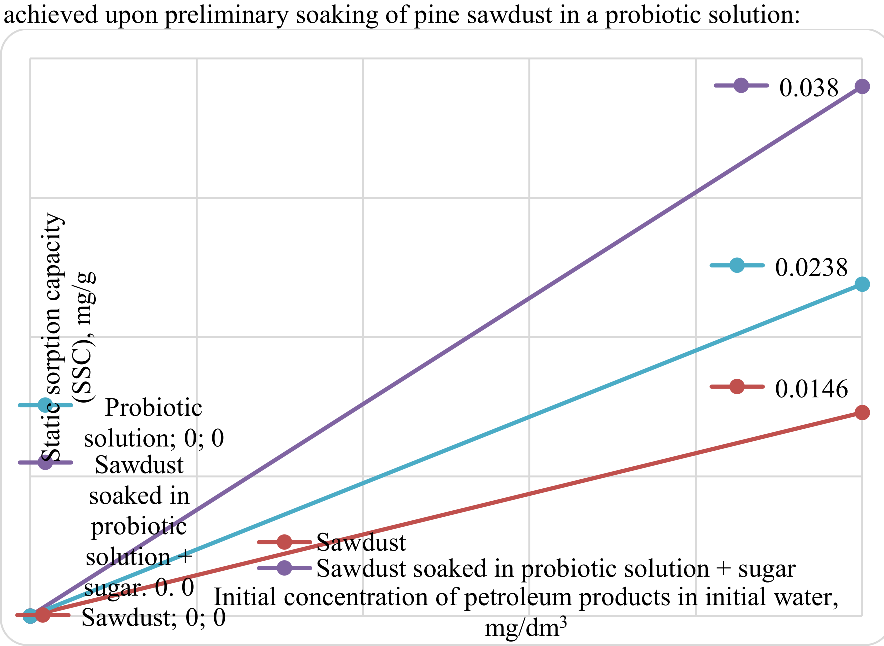

Fig. 1. Sorption isotherms in different methods of sorbent or aqueous solution of petroleum products treatment.

The results of thesorption study in a dynamic mode are summarized in Tables 2 and 3, from which it can be seen that when the sawdust is soaked in a probiotic, the sorption of petroleum products increases compared to sorption on pure sawdust, and the maximum cleaning effect is 48.68%.

Table 2. Dynamic exchange capacity when filtered through a layer of sawdust.

Filtering through a layer of sawdust			
Sample volume, cm^3	Final concentration of petroleum products, mg/dm^3	Dynamic sorption capacity (DSC), mg/g	Treatment effect, %
50	discharge	-	-
100	4.5	0.016	15.09
100	4.6	0.014	13.21
100	4.34	0.019	18.11
100	4.29	0.020	19.06
100	4.31	0.020	18.68
150	4.23	0.032	20.19
150	4.18	0.034	21.13
100	4.32	0.020	18.49
100	4.47	0.017	15.66
100	4.65	0.013	12.26
100	4.57	0.015	13.77
100	4.71	0.012	11.13
100	5.03	0.005	5.09
100	5.05	0.005	4.72
100	5.19	0.002	2.08
150	5.23	0.002	1.32
150	5.3	-	-
DSC=0.135 mg/g; FDSC =0.245 mg/g			

Table 3. Dynamic exchange capacity when filtered through a layer of sawdust soaked in probiotics.

Filtration through a layer of sawdust soaked in probiotics			
Sample volume, cm^3	Final concentration of petroleum products, mg/dm^3	Dynamic sorption capacity (DSC), mg/g	Treatment effect, %
100	2.98	0.046	43.77
100	2.93	0.047	44.72
100	2.72	0.052	48.68
100	3.05	0.045	42.45
150	3.46	0.055	34.72
150	3.6	0.051	32.08
150	3.83	0.044	27.74
150	4.08	0.037	23.02
150	4.35	0.029	17.92
150	4.79	0.015	9.62
150	5.11	0.006	3.58
150	5.3	-	-
DSC =0.145 mg/g; FDSC =0.427 mg/g			

The dynamic sorption patterns are reflected by the output curve, which is the dependence of the change in the concentration of petroleum productsin aqueous solutionsamples at the outlet from the volume of the sample of the aqueous solution released from the column from the start of the experiment to the breakthrough of petroleum products. The graphs are shown in Fig. 2.

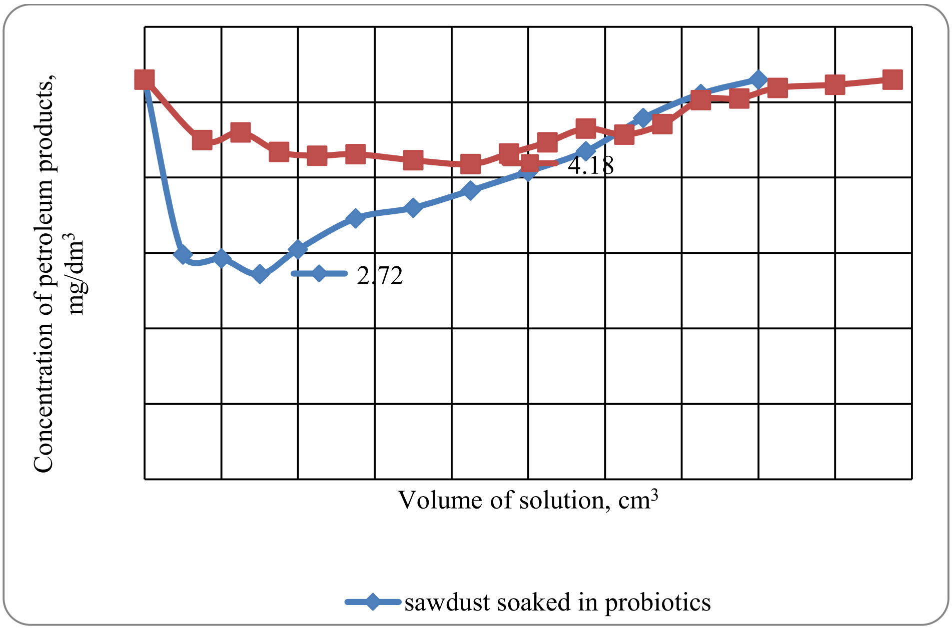

Fig. 2. Dependence of oil product concentration on the flowing volume of water solution for different samples.

The complex sorbent extracts 2.014 times more of petroleum products from the aqueous solution than the pure sawdust and has a higher absorption rate.

5 Discussion

Based on the results of this study, a filtering scheme was proposed using the example of surface wastewatertreatmentfrom a 17hectare oil depot, located near the city of Surgut (Tyumen region). The petroleum depot has 3 tank parks consisting of 5 steel vertical tanks for storing oil in bunds, with a volume of 2000 m^3 (diameter 15 m) each. The quantitative characteristics of a surface runoff, calculated according to modern regulatory documents, are presented in Table 4. The volume of water taken for treatment is calculated as the maximum daily volume of melt water, taking into account 10% of the reserve.

Table 4. Surface runoff quantities.

Parameter	Volume, m^3
Average annual volume of rainwater	38027
Average annual volume of meltwater	21273
Average annual volume of sprinkling water	2665
Average annual volume of surface wastewater	61965
Amount of rain runoff from the calculated rain	780
Maximum daily volume of meltwater	952
Volume of water for treatment	**1050**

A low-cost option for surface wastewater treatment is purification using local filtration facilities, which are a standard sewer well with a filter cartridge mounted inside. The filter cartridge is an easy-to-replace, durable plastic cylindrical device that has the appropriate type of loading depending on the purpose. The design of the filters allows them to be used in bulk (non-pressure) mode in the absence of a power source [16].

Filters loaded with pine sawdust should be installed outside the tank farm, at the end of three branches of the rain network. We can find the height of the filter cartridge of the real installation using formula (3) [17]:

$$H_f = \frac{1}{\beta} \cdot \vartheta_f \cdot ln\ ln\ \left(1.5 \cdot \frac{C_{initial}}{C_{final} \cdot (1-\varepsilon)}\right) \cdot C \quad (3)$$

whereβ = the mass transfer coefficient (formula 4); $\vartheta f = 0.5$ cm/s is filtering speed; $C_{initial} = 5.3$ mg/dm^3 is the initial concentration of oil products; $C_{final} = 2.72$ mg/dm^3 is concentration of petroleumproducts at the outlet; ε= 0.2 is the porosity of the loading layer; C = 1.5 is the safety coefficient.

Masstransfer coefficient is defined as [17]:

$$\beta = -\frac{1}{\tau} \cdot ln \frac{C_{instant}}{C_{initial}} \quad (4)$$

whereτ=50 sec is instantaneous breakthrough time; $C_{instant}=3.05$ mg/dm^{3}isinstantaneousbreakthrough concentration.

$$\beta = -\frac{1}{50} \cdot ln \frac{3.05}{5.3} = 0{,}011, \quad (5)$$

$$H_f = \frac{1}{0.011} \cdot 0.5 \cdot ln\ ln\ \left(1.5 \cdot \frac{5.3}{2.72 \cdot (1-0.2)}\right) \cdot 1.5 = 88\ m = 900\ mm. \quad (6)$$

The effective area of the filter cartridge is calculated on the basis of the maximum flow rate of surface runoff per second:

$$F = \frac{Q}{\vartheta_f} = \frac{0.004}{0.005} = 0.8\ m^2, \quad (7)$$

where Q = 14.6 m^3/h = 0.004 m^3/s is the flow rate per second of waste water per 1 filter; $\vartheta f = 0.005$ m/s is the filtering rate.

With an area of 0.8 m^2, the diameter of the filter is 1000 mm. The general structure of the filtering facility for surface runoff treatment is shown in Fig. 3.

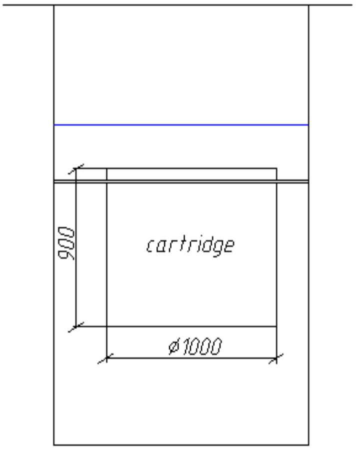

Fig. 3. Treatment of surface runoff by filter wells.

The market value of pine sawdust in the city of Tyumen is 350 rubles per m^3 of raw material. Based on calculations, in this case, 1 filter requires 0.71 m^3 of sawdust, which in monetary terms is 250 rubles for each filter. The price of 1 dm^3 of PipPlusWATER probiotic is 1070 rubles. When the concentration of the probiotic solution is 0.05 mg/dm^3, 15.5 ml of pure probiotic is needed to activate the sawdust loading in the amount of 0.71 m^3, which will cost 16.6 rubles for each filter. Sugar and consumption are negligible. The cost of the finished load with 3 working filters will be 800 rubles.

6 Conclusions

Based on the results of the study of the process of the PipPlusWATER probiotic agent influence on the efficiency of sorption purification, the following conclusions can be drawn:

1. The combined use of pine sawdust with a probiotic increases oil absorption by 2,014 times compared to the use of pure sawdust. At the same time, the maximum removal of petroleum products was achieved by 48.68% (with sorption with pure sawdust by 21.13%).
2. The spent sorbent can be recovered as an additional source of heat by combustion in the form of fuel briquettes and has minimal secondary environmental pollution.
3. This technology is recommended for use in pressure and non-pressure sorption filters for the purification of wastewater containing petroleum products.
4. The cost of 1 m^3 activated sawdust is 375 rubles.

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