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Purification of Oil-Contaminated Wastewater with a Modified Natural Adsorbent

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ABSTRACT
Water purification from oil and oil products is the final stage of its preparation before injection into the oil reservoir. Natural sorbents are preferred over synthetic ones for use on drilling platforms. They have minimal negative impact on the environment as well as constitute renewable and biodegradable resources. Several adsorbents, based on various natural materials, which could be potentially used for wastewater treatment systems on drilling platforms, were selected. Comprehensive studies of natural sorbents were conducted to determine the possibility of their use as a filtration material for wastewater treatment from oil and oil products on the drilling platforms. As a result of laboratory studies, it was found that the most promising solution is the use of several types of nut shells, which showed the best ratio of abrasion resistance and adsorption characteristics. Among the studied shell samples, pecan shells showed the highest oil product adsorption. As a result of the temperature treatment of the sorbent, it was possible to increase the value of oil products adsorption twice and the value of adsorption activity by almost 13 times without reducing the strength characteristics. It was found that it is advisable to carry out carbonization at a temperature of 400°C.

Keywords: natural adsorbent, oil-contaminated water, filtration treatment, nutshell, adsorbent modification

INTRODUCTION

Offshore oil and gas production is associated with maintaining reservoir pressure by reservoir, ballast and seawater injection. Injected water purification from oil and oil products is an important stage of its preparation. Adsorption is the most common method used for this purpose.

Filters for water purification from the residual content of oil and oil products are cylindrical vertical tanks filled with granular filter material. The key factors when deciding on which sorbent type to use include its composition and regeneration peculiarities on the drilling platforms, which do not involve the use of reagents or frequent replacement of the filter. Therefore, the filter material must have not only high adsorption capacity but also suitable strength characteristics.

Natural sorption materials are preferable to synthetic ones since they belong to renewable and biodegradable resources. They also have minimal negative impact on the environmental components under the conditions of their use on the drilling platforms [Bykova and Pashkevich 2020].

World experience offers many potential adsorbents of natural origin, currently used in enterprises for wastewater treatment from oil and oil products. Due to the variety of sorption materials, it is relevant to choose the most suitable sorbents for the operating conditions of the water treatment system on drilling platforms, taking into account the main characteristics of the adsorbents and methods of their regeneration.

Therefore, this work was aimed at conducting comprehensive studies of natural sorbents to determine the possibility of their use as a filtration material for wastewater treatment from oil and oil products on the drilling platforms.

MATERIALS AND METHODS

Clays, diatomites, and silicates have recently become widely used as inorganic natural adsorbents, due to their low cost and the possibility of production in large volumes [Sirotkina and Novoselova 2005]. Adsorbents based on coal, cellulose, and wood are the most common use of organic natural sorbents [Kotova et al. 2016].

Coal-based adsorbents are high-carbon polymers, the pore structure of which provides high-efficiency extraction of high-molecular compounds from water, including oil and oil products [Pashkevich et al. 2017; Trusova 2014]. Cellulose-derived aerogels are super light solid materials with high porosity and large surface area, which makes them valuable oil sorbents [Liu et al. 2016].

Carboxymethylated pinewood adsorbents derived with the help of the suspension method have a high adsorption capacity for oil and oil products [Kogan 2016]. Regeneration and multiple reuses of these adsorbents are provided by oil-degradation bacteria, which are applied to the surface of granules [Denisova 2017]. Furthermore, shells of various types of nuts are increasingly often used as adsorbents, due to the possibility of removing suspended solids and oil products from wastewater at high flow rates in combination with the ease of backwashing [Odintsova 2010]. Thus, some adsorbents, based on various natural materials, which could be potentially used for wastewater treatment systems on drilling platforms, were selected for comprehensive studies (Table 1).

The possibility of using adsorbent under the conditions of drilling platforms was determined, first of all, by its physical mechanical, physical chemical and chemical properties such as abrasion resistance, hardness, bulk density, holding capacity, water adsorption, oil products adsorption, full saturation time, surface area, total carbon. In order to determine the specified characteristics of the selected adsorbents, their complex laboratory studies were carried out using various standard methods and techniques presented in Table 2.

In order to increase the oil product adsorption of the most promising sorbent for further research (pecan shells), its carbonization was carried out [Temirhanov et al. 2012]. Heat treatment was carried out in a muffle furnace in the temperature range of 200–450ºC with a step of 50ºC for 45 minutes. Afterwards, the holding capacity and oil products adsorption were determined for each sample. All the main characteristics were also determined for pecan shells, modified at 400°C.

Dynamic sorption capacity was determined for the original and modified sorbent at temperatures of 350ºC, 400ºC, and 450ºC, by modeling the process of oil-contaminated wastewater purification. A model solution of oil-contaminated water was passed through the adsorbent layer in the sorption column. The concentration of oil products in adsorbent and purified water were determined by using a fluorometric method. It is based on the extraction of oil products from the sample by a low-polar solvent (hexane) and measuring the fluorescence intensity of the extract with the "Fluorate-02" fluorometer (Russia) [PND F 14.1: 2: 4.128-98].

Table 1. Natural potential adsorbents for wastewater treatment from oil and oil products

Adsorbent name	Adsorbent type
British walnut shell	Walnut shell
Black American walnut shell	
Pecan shell	
English walnut shell	
Kausorb-221	Activated coal
Dausorb	
Sorber-15	
Adsorbent MS	Silicates
MFU	
Adsorbent AS	
ODM-2F	Flask
Profsorb Ultra	Expanded vermiculite
Glauconite	Glauconite

Table 2. Methods and techniques used to determine the main properties of adsorbents

Characteristic of the adsorbent	Method / technique of studying
Abrasion resistance	GOST 16188-70 [6]
Bulk density	GOST 16190-70 [7]
Hardness	The Mohs Hardness Scale
Holding capacity	Gravimetry [9]
Water adsorption	ASTM F 716 [3]
Oil products adsorption	ASTM F 716 [3]
Full saturation time	ASTM F 716 [3]
Adsorption activity	GOST 4453-74 [8]
Surface area	B.E.T. [1]
Total carbon	IR spectrometry [2]

RESULTS AND DISCUSSION

The results of studies of the main characteristics of the selected adsorbents are presented in Tables 3. The Dausorb, Profsorb Ultra, MS, AS, Sorber-15, glauconite, and Kausorb-221 adsorbents showed high values of oil products adsorption. However, their use as adsorption materials in fine filters is limited by not suitable values of abrasion resistance and, in some cases, low values of hardness on the Mohs scale. The usage of the MFU and ODM-2F adsorbents for wastewater purification from oil products is limited by low values of oil products adsorption. Among the studied sorbents, a combination of high values of abrasion resistance and suitable values of adsorption of oil products was noted in the shell of various types of nuts (Table 3). The most promising for further research was the pecan shell, which has the largest surface area and, as a consequence, the absorption capacity of oil products among other adsorbents based on nutshells. However, as an oil adsorbent for wastewater treatment in drilling platforms, its absorption capacity is insufficient.

The results of studies of holding capacity and oil products adsorption of modified pecan shells are presented in Figures 1 and 2.

According to the results of the conducted studies (Fig. 1, 2), it was found that the oil products adsorption of pecan increases after carbonization in the temperature range of 200–300°C and then with a further temperature increase reaches a constant value. At the same time, modification of the adsorbent at temperatures below 400°C leads to a decrease in its holding capacity.

The results of the study of the dynamic sorption capacity of the original and modified at temperatures of 300–450ºC adsorbent based on pecan shells are presented in Table 4. The dynamic capacity of the adsorbent modified at temperatures of 350–400ºC increases significantly in comparison with the unmodified one; with a further temperature increase, it is insignificant. In this way, it is most advisable to carbonize pecan shell at 400ºC. The main characteristics of the adsorbent based on the pecan shells modified at a temperature of 400ºC are presented in Table 5.

The study of the physicomechanical, physicochemical and chemical properties of the pecan shell modified at a temperature of 400ºC showed a slight decrease in abrasion resistance, which

Table 4. Oil products concentration in the adsorbent after model oil-contaminated water purification

Adsorbent name	Oil products concentration in the adsorbent after water purification, mg/g
Pecan shells	24.10
Pecan shells – 350	28.15
Pecan shells – 400	35.11
Pecan shells – 450	35.26

Table 3. Physical mechanical, physical chemical and chemical properties of the adsorbents

Adsorbent name	Characteristic of the adsorbent										
	Abrasion resistance, %	Bulk density, g/dm^3	Water adsorption, g/g	Oil products adsorption, g/g	Adsorption activity, mg/g	Total carbon, %	Full saturation time, min / g/g		Holding capacity g/g	The Mohs hardness scale s	Surface area, m^2/g
British walnut shell	99.97	660.0	0.90	0.677	3.6	51.3	30	0.682	0.624	2-3	7.7
Black American walnut shell	99.88	652.5	0.81	0.683	6.6	52.1	25	0.698	0.449	2-3	7.3
Pecan shell	99.97	637.5	0.88	0.797	2.6	54.7	20	0.798	0.715	2-3	11
English walnut shell	90.88	685.5	0.90	0.666	3.6	52.5	25	0.667	0.579	2-3	7.6
Dausorb	67.78	446.1	1.28	0.801	21.3	80.8	15	0.801	0.510	2-3	669
Profsorb ultra	51.95	130.8	3.17	3.159	28.1	0.36	12	3.158	2.820	< 1	15
Adsorbent MS	79.51	1594.5	0.28	0.237	1.9	0.12	9	0.237	0.250	3-4	6.7
MFU	95.23	1220.0	0.35	0.337	2.9	0.20	6	0.338	0.330	6-7	3.8
ODM-2F	99.05	716.8	0.54	0.552	6.6	0.13	12	0.551	0.380	2-3	43.1
Adsorbent AS	50.88	496.0	1.39	1.251	12.4	0.12	12	1.250	1.040	2-3	109
Sorber-15	64.00	461.8	1.13	0.693	18.9	83.7	6	0.691	0.570	2-3	763
Glauconite	53.40	1064.5	0.27	0.211	1.3	0.12	3	0.210	0.160	3-4	37
Kausorb-221	85.11	529.0	0.82	0.513	15.0	94.4	3	0.510	0.280	2-3	693

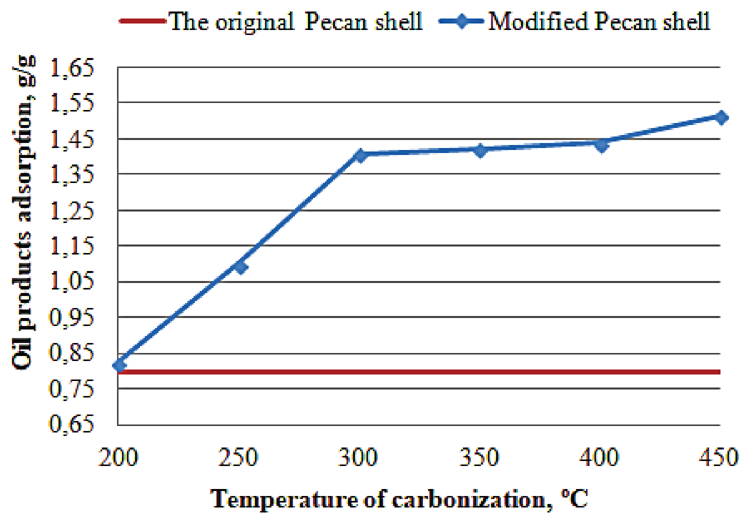

Figure 1. Dependence of oil products adsorption of pecan shell on the carbonization temperature

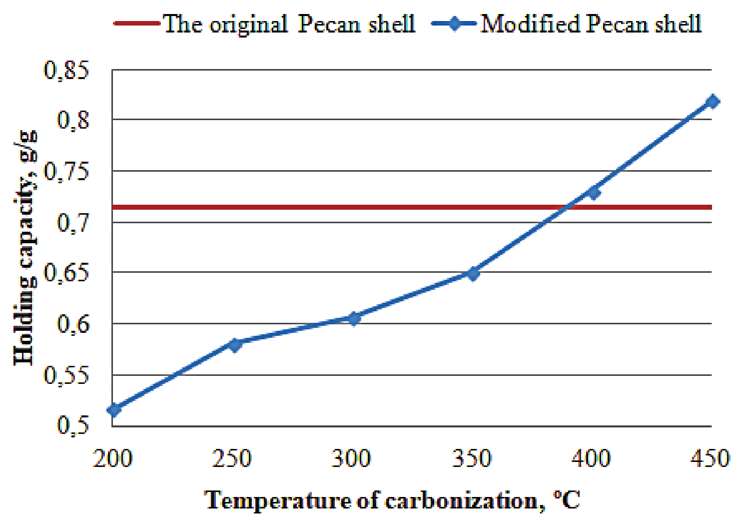

Figure 2. Dependence of holding capacity of pecan shell on the carbonization temperature

Table 5. Physicomechanical, physicochemical and chemical properties of the pecan shells modified at 400°C

Adsorbent name	Characteristic of the adsorbent	Units	Value
Pecan shells – 400	Abrasion resistance	%	96.21
	Bulk density	g/dm^3	518.30
	Water adsorption	g/g.	1.17
	Oil products adsorption	g/g	1.403
	Adsorption activity	mg/g	36.25
	Total carbon	%	1.17
	Holding capacity	g/g	0.730
	The Mohs hardness scale	–	2–3

does not limit its usage under the conditions of drilling platforms. The adsorption of petroleum products has doubled, the adsorption activity has increased almost 13 times, the retention capacity has remained the same, which is consistent with the results of dynamic tests of the adsorbent.

CONCLUSIONS

As a result of laboratory studies of the physical-mechanical, physical-chemical, and chemical properties of adsorbents based on various natural materials, it was found that use of various types of nutshells, which showed the best ratio of abrasion resistance and adsorption characteristics is the the most promising. Among the studied shell samples, pecan shells showed the highest oil products adsorption. As a result of the temperature treatment of the sorbent, it was possible to increase the value of oil products adsorption twice, and the value of adsorption activity by almost 13 times without reducing the strength characteristics. It was found that it is advisable to carry out carbonization at a temperature of 400°C for 45 minutes. Further studies of the regeneration process of the selected sorbent, as well as methods of its utilization, are very promising.

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