

Studying the Mechanism of Using Grain Husks to Remove Dissolved Petrochemicals from Test Water

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Abstract: This paper presents our research on removing dissolved petrochemicals from water by sorption using vegetable matters. For this purpose, we used grain crop husks and their modifications as sorbents. We prepared test solutions and experimented on sorption in static and dynamic conditions. Grain husks were modified chemically and thermally. The experiments showed that modifying with 1% sulfuric acid (SA) solution and heating allow increasing the adsorption capacity by 10-15 % and 35-40 %, respectively. Dependencies obtained for the adsorption capacity of original and modified samples indicate that the isotherm of adsorbing the dissolved petrochemicals by grain husks is described by the Freundlich equation, which is evidence of a mixed-diffusion sorption mode. To identify the filter bed operation time, we measured the dynamic exchange capacity of five filter bed samples. According to various combinations of modified samples proposed as filter bed, heat-treated oat husks : acid-modified oat husks : heat-treated oat husks at a ratio of 4:6:4 at a water flow rate of 10-15 cm³/min allows maintaining the filter operability of up to 6 hours. Oil gets adsorbed at WGH in the mixed-diffusion mode, while the internal diffusion is a stage that limits adsorption according to the activation energy estimates (6-20 kJ/mol). This is due to the structural features of cellulose and lignin contained in sorption materials (SM) that have a complex amorphous crystalline structure. Presumably, petrochemicals (PC) are adsorbed on the surface of SMs at the beginning of adsorption process, forming a monomolecular layer, and then, with increase in concentration, start penetrating into internal pores and filling out the amorphous crystalline zones in the composite structure.


1 INTRODUCTION


Oil production rates and oil refining industry development are increasing year on year both in Russia and around the globe. Despite the ongoing environmental protection measures, oil and petrochemicals cause significant damage to the environment, both during the normal course and resulting from various accidents. The hydrosphere is especially affected, as approximately 10-15% of petroleum hydrocarbons entering water bodies dissolve. The composition of the oil and the turbulent

regime of water masses influence upon generating of oil emulsions (Davydova, Tagasov, 2004). Nowadays, there is a large number of methods to remove oil from aqueous media: Mechanical, physical, biological, etc. (Peregudov, 2021, Tatarintseva, Bukharova & Ol'shanskaya, 2014). The sorption method is essential due to its advantages, such as removal of both dissolved, emulsified, and immiscible petrochemicals from water. In addition, the sorption method involves a wide range of raw materials, including synthetic polymer sorbents to agricultural wastes (Stepanova,

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Alekseeva & Khafizova, 2021, Malyshkina, Vyalkova & Osipova, 2019). Despite the diverse market, search for an effective, selective, and also cheap sorption material (SM) is an important task. In this regard, we performed a study of water purification by removing dissolved petrochemicals using modified samples of wheat grain husks (WGH), barley grain husks (BGH), and oat grain husks (OGH), all being agricultural wastes.

2 MATERIALS AND METHODS

We strongly encourage authors to use this document for preparation. This study is aimed at research in removing dissolved petrochemicals (PC) from water by plant materials, based on grain crop husks (GCH) and their modifications. To achieve this goal, the following tasks were solved:

- Modifying SMs with an SA solution and heating the GCH samples;
- Preparing test solutions (TS);
- Determining the static (A) and dynamic exchange capacity (DEC) of original and modified materials;
- Examining the mechanism of adsorbing dissolved PCs by the SMs obtained; and
- Checking the applicability of SM as a filter bed.

Husks were modified chemically as follows: We took 10 g of GCH and 200 cm³ of 1% SA solution and stirred them for 60 minutes. Upon the contact completion, we separated the sample and washed it repeatedly with distilled water until the medium became neutral. Then we dried the samples to constant weight in a dry-heat oven at a temperature of 100 ± 5 °C.

We heated the GCH samples weighing 20 g in a dry-heat oven with forced convection, which ensures temperature uniformity throughout the oven chamber, at a temperature of 150-160°C for 15-20 minutes, with a constant stirring.

We prepared TSs containing dissolved PC concentrations of 8.76, 26.3, 43.84, 65.7, and 87.68 mg/dm³, respectively (approved by Deputy Chairman of the State Committee of the Russian Federation for Environmental Protection, 2000).

Water was purified from dissolved PCs under static conditions as follows: We placed the pre-weighed portions of the GCH under study, 1 g each, into five flat-bottomed flasks with the capacity of 250 cm³ and poured TS into the flasks, 100 cm³ each. The flasks, with the portions of the samples and the solutions inside, were tightly closed with stoppers and shaken vigorously for one hour. Then we removed

GCHs and computed the residual concentrations of petrochemicals in the filtrates according to the methods (Deputy Chairman of the State Committee of the Russian Federation for Environmental Protection, 2000, Deputy Chairman of the State Committee of the Russian Federation for Environmental Protection, 1997, Stepanova, Alekseeva & Khafizova, 2020).

To study the dynamic exchange capacity (DEC), we used filters of various fillings. Contaminated water was prepared with the initial concentration of 0.5 ± 0.2 mg/dm³ in a vessel with the capacity of 5 dm³. To achieve a uniform concentration of oil in the water, we stirred it for 60 minutes. Then we found the initial concentration of PCs in water. The water flow rate was set at 0.003 m³/min and passed through a glass column with the diameter of 4.5 cm, filled with samples (Table 2).

To estimate the filter bed operation time, we sampled water and evaluated the residual oil content in it at certain time intervals (every 20 minutes). The experiment was carried out up to the point of "breakthrough."

Dynamic exchange capacity (DEC, mg/g) was calculated by the formula:

$$DEC = \frac{V \cdot C_e}{m}, \quad (1)$$

where m is the mass of the LCCM portion, g;
 C_e is equilibrium concentration, mg/dm³; and
 V is the volume of the model solution, dm³

3 RESULTS

As a result of the experiments carried out, we obtained the dependencies of the adsorption capacity of native GCHs and of ones modified with the SA solution (GCH + SA) and thermally modified wheat grain husks (TMWGH) on concentration (Fig. 1).

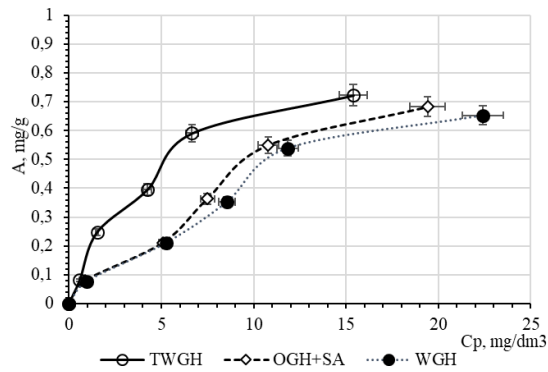


Figure 1: Dependence of the adsorption capacity of WGH samples on the concentration of petrochemicals in water

To study the curves and the mechanism of adsorbing the dissolved PCs from water in more detail, we computed the Langmuir and Freundlich equations. Table 1 shows the results of the computations on the original and modified samples of OGH, WGH, and BGH, including thermally modified oat grain husks (TMOGH).

Table 1: This caption has more than one line so it has to be set to justify.

SM Samples	Model by Langmuir $A = \frac{A_{\infty} \cdot K \cdot C}{(1 + K \cdot C)}$		
	K_L	A_m	R^2
WGH	1.1208	0.0202	0.6016
WGH+SA	1.2786	0.0205	0.6264
TMWGH	1.7932	0.0165	0.756
OGH	1.1436	0.0237	0.468
OGH+SA	1.1105	0.0221	0.5283
TMOGH	1.6094	0.0292	0.4731
BGH	1.3399	0.0230	0.421
SM Samples	Model by Freundlich $A = K \cdot C^n$		
	K_f	N	R^2
WGH	2.8164	1.4162	0.8976
WGH+SA	3.3822	1.5494	0.9383
TMWGH	5.1940	1.4275	0.9594
OGH	3.0186	1.6396	0.7799
OGH+SA	2.5562	1.5085	0.9585
TMOGH	3.6050	2.2305	0.8998
BGH	3.3067	1.6647	0.784

As it follows from Table 1, the isotherm of dissolved PC adsorption from water by samples of lignin cellulose containing materials (LCCM) is most accurately described by the Freundlich equation.

Since modifying the GCH samples contributes to an increase in the static adsorption capacity and there is a need for increasing the efficiency of the filters, we studied the DEC of the GCH samples prepared in

various combinations (Table 2). For this purpose, we proposed five filters with different SM ratios and TS usage rates of 10-15 cm³/min.

Table 2: Parameters of filling the filters to remove the dissolved PCs.

Filter No		Component	Weight, g
1	Lower layer	TMOGH	4.90
	Middle layer	OGH+SA	6.11
	Upper layer	TMOGH	4.49
2	Lower layer	WGH+SA	2.55
	Middle layer	BGH+SA	4.72
	Upper layer	WGH+SA	2.99
3	Lower layer	TMOGH	3.96
	Middle layer	OGH+SA	6.18
	Upper layer	TMOGH	4.50
4	First (lower) layer	BGH+SA	3.90
	Second layer	OGH+SA	2.00
	Third layer	WGH+SA	5.00
	Forth layer	TMOGH	1.80
5	Lower layer	WGH+SA	2.40
	Middle layer	TMOGH	4.50
	Upper layer	WGH+SA	2.90

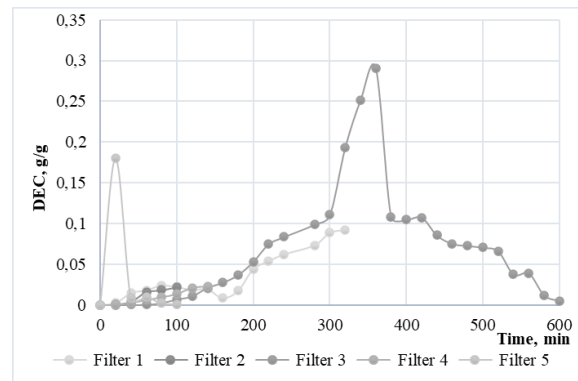


Figure 2: Dependence of the adsorption capacity of WGH samples on the concentration of petrochemicals in water

Figure 2 shows that Filter 3 has the longest operation time with the ratio of TMOGH : OGH+SA : TMOGH = 4: 6: 4. This ratio is the most optimal among the investigated ones. Thus, we can recommend this ratio as a filter filling, since it ensures the longest operation time and has the highest DEC.

4 DISCUSSION

Studying the WGH adsorption capacity in relation to dissolved PCs under static conditions shows that the curves (Fig. 1) of the samples are of a stepped nature, which indicates the presence of both micro- and macropores. According to the Gils classification, all isotherms can be categorized to L (Langmuir) class. At the initial stage, isotherms of this class are concave with respect to the concentration axis. Moreover, this type is characteristic of polymolecular adsorption and adsorption of surfactant associates (Tovbin, 2013). In this case, the adsorption capacity of TMWGH is higher than that of the original samples and those treated with a sulfuric acid solution.

With GCHs, oil is adsorbed in a mixed-diffusion mode, with the internal diffusion as a stage limiting the adsorption process, according to the activation energy estimates (6-20 kJ/mol) (Shaidullina, Stepanova 2017). Probably, the reason lies in the structural features of cellulose and lignin, which are part of SMs and have a complex amorphous-crystalline structure. Presumably, at the beginning of the adsorption process, PCs are adsorbed on the surface of SMs, forming a monomolecular layer; later, with increasing concentration, they start penetrating into the internal pores, filling the amorphous-crystalline zones of the composite structures (Alekseeva, Stepanova, 2019). Modifying the samples allowed us to increase the adsorption capacity by 10-15 % with acid treatment and by 35-40 % with heat treatment. It is possible to conclude that the modification has a positive effect on the adsorption properties of the presented material in relation to oil.

5 CONCLUSION

Within this research, we prepared TSs and examined the static and dynamic adsorption capacity of original and modified lignin and cellulose containing material samples in relation to dissolved petrochemicals. It is shown that the grain crop husks modification allows increasing the adsorption capacity of vegetable waste in relation to petrochemicals, namely: By 10-15% with acid treatment and by 35-40% through heating. We also found that the isotherm of adsorbing dissolved petrochemicals from water by the samples of lignin cellulose containing materials is most accurately described by the Freundlich equation. GCH-based oil adsorption runs in a mixed-diffusion mode, while internal diffusion is a stage that limits the adsorption process, according to the calculated activation energy figures. To increase the efficiency

of removing petrochemicals from water, we propose various combinations of modified samples of vegetable matters at different ratios. We consider the ratio of TMOGH: OGH+ SA: TMOGH = 4: 6: 4 to be the most optimal, with the filter bed operation time reaching 6 hours. Using this type of material, we solve two problems: the removal of petrochemical substances from water and the rational use of plant waste.

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