

Studying the Efficiency of Treatment Model Mixtures of Petroleum Products with the Modified Sorbent Made of Ash-and-Slag During Dynamic Sorption

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ABSTRACT

Experimental studies on the dynamic sorption of model mixtures containing petroleum products were performed. The subject of the study was the modified sorbent from the ash-and-slag wastes accumulated in the ash dump of the Novochoerkassk State District Power Plant (SDPP) (Russia, Novochoerkassk, Rostov Region), obtained using the method of ash removal. The quantity of the sorbent for each model solution was fixed at 5.0 g. The model solutions in the amount of 1 dm³ were passed through a column filled with the modified sorbent at constant filtration rate $w = const$ with filtrate takeout of 0.1 dm³/min. The pH value of the solution, which is advisable for extracting petroleum products, was determined experimentally. For this purpose, the model solutions, containing 100 mg/dm³ of petroleum products with pH = 1.65, 4.01, 6.86, 8.12, 9.18, and 11.34, were prepared. The optimum pH value of the solution was considered pH = 7.5. The content of petroleum products in the filtrate in all experiments was determined using IR spectrometry. The working range of water pollution with petroleum products was determined on a series of model solutions containing petroleum products in the range between 0.5 and 10 mg/dm³ with the increment of 0.5, between 10 and 100 mg/dm³ with the increment of 10, and between 100 and 1,000 mg/dm³ with the increment of 100. The maximum extraction of petroleum products from the solution was 88.23%. The applicability of the Henry's law to the range of petroleum products concentrations in the filtrate of 50 mg/dm³ was confirmed. The adsorption equilibrium constant (Henry's law constant) was determined experimentally. The effect of the natural freshwater matrix on the degree of petroleum products extraction was studied; no significant effect on petroleum products sorption was found. A conclusion was made that the sorbent can ensure the efficiency of water purifying from petroleum products of no less than 85% in the range of pollution between 5 and 300 mg/dm³.

Keywords: ash-and-slag, thermal power plant, sorbent, sorption dynamics, the efficiency of petroleum products extraction

INTRODUCTION

Fly ash and ash-and-slag, called together ash-and-slag wastes (ASW), or simply ash-and-slag, are the large-scale wastes of thermal power plants that use solid fuel (coal). Huge areas – ash dumps (ash-and-slag waste dumps) – are used for their storage. ASW are mainly transported to the ash-and-slag waste dumps with buger pumps after mixing ASW with water. As a result, water pulp is formed. This method of waste transportation is called hydraulic ash disposal (HAD).

In Russia, the amount of accumulated ash-and-slag waste is equal to billions of tons, and the area occupied by them reaches thousands of hectares of land [Cherentsova, 2013]. Many works were devoted to using ASW as an adsorbent in wastewater treatment for removing phosphates, heavy metals, organic pollutants, phenols, and dyes [Cheung, Venkitachalam, 2000; Safaa, 2013; Yamada et al., 1986; Dabi, Patwa, 2015]. It was suggested to use ASW as an adsorbent for treating the wastewater contaminated with petroleum products [Shishelova et al., 2008]. The studies

on the ASW hazard class at the Novochoerkassk SDPP performed by the authors showed that the dry ash and slag hazard class for the environment was between III and IV (low-hazard) [Korotkova et al., 2017, Bushumov et al., 2018]. The ash and slag accumulated at ash dumps through HAD belong to the environmental hazard class V (virtually not hazardous) [Korotkova et al., 2018].

This work is devoted to studying the adsorbent obtained by modifying the ASW from the Novochoerkassk SDPP accumulated at dumps by hydraulic ash disposal for removing the oil products from wastewater. Dynamic sorption was performed by means of model solutions with various concentrations of petroleum products acting as wastewater.

RELATED WORK

The use of adsorbents for extracting components from solutions has been known since the ancient times. Fundamental theoretical generalizations have been developed: theory of thermodynamics of adsorption, the fundamentals of calculating the adsorption and desorption kinetics, and the theory of mass transfer in adsorption processes [Keltsev, 1984].

Sorbents of natural (natural organic materials) and synthetic origin (synthetic organic materials), as well as sorbents with properties changed by modification, e.g., adding a component, grinding, or calcination at high temperatures, are used to remove the petroleum products from the water. Such sorbents are called petroleum sorbents. In wastewater, the petroleum products are contained in free, emulsified, and dissolved states. The mechanisms for removing petroleum products are physical surface adsorption and bulk adsorption (absorption by the entire volume of the sorbent) [Veprikova et al., 2010].

The sorbent efficiency is assessed by sorbent petroleum capacity under the dynamic conditions by passing the polluted solution through a compacted layer of the sorbent in a column until the complete saturation of the sorbent [Komissarenkov, Fedorova et al., 2015]. Adsorption equilibrium, which allows determining the amount of the sorbent (or the thickness of the adsorptive layer) required for the maximum possible efficiency of solution treatment is also an important characteristic [Keltsev, 1984, Makarevich, Bogdanovich, 2015]. Various kinetic models are studied to understand and explain the mechanism of adsorption [Gorme et al., 2010].

In this work, the dynamics of sorption of the model solutions containing petroleum products were studied. The efficiency of extracting petroleum products by means of a modified sorbent made of the ASW from the Novochoerkassk SDPP accumulated by hydraulic ash disposal was studied.

METHODS

The content of petroleum products in the filtrate was determined by means of IR spectrometry with PCM-025 concentration meter (P – petroleum products), and double-checked using PC-3 concentration meter to remove random measurement errors according to environmental regulatory document of the federal level (ERD F) 14.1:2:4.5-95. The studied amounts of filtrates were placed in a 2 dm³ separating funnel; diluted sulphuric acid was added at the rate of 2 cm³ of acid per 100 cm³ of the filtrate. The vessel in which the filtrate was held was rinsed with 10 cm³ of carbon tetrachloride, which was later drained into a separating funnel. Another 20 cm³ of carbon tetrachloride were added to the filtrate, and extraction was performed with vigorous stirring for four minutes. Afterwards, the emulsion was left to settle for 10 minutes. The organic layer was drained into a 100 cm³ measuring cylinder and the extract was dehydrated with 5 g of anhydrous sodium sulfate until it lightened up, followed by decanting of the extract into a 50 cm³ measuring cylinder in order to determine the exact volume. Next, the extract was passed in a chromatography column through a layer of activated aluminum oxide for removing the interfering polar compounds and residual water. The prepared extract was placed in a cuvette of a concentration meter for subsequent detection of C-H bonds in the area of IR radiation, with the aim of obtaining the analytical signal that characterized the quantitative content of the studied components.

RESULTS AND DISCUSSION

The object of the study was the modified sorbent obtained from ASW of the Novochoerkassk SDPP, accumulated at ash dumps by hydraulic ash disposal. The waste was formed by burning coal of the Donetsk culm. The sorbent was obtained in two stages by heating and exposure: in the first

stage, the ash-and-slag waste was heated to 110°C and kept at this temperature for 30 minutes; in the second stage, it was heated to 600°C and kept at this temperature for 40 minutes. These stages allowed to increase the internal pore volume and to obtain the modified sorbent. The physicochemical properties of the sorbent were experimentally determined by the authors: bulk density of 0.666 g/cm³; ash content of 99.5 %; abrasion of 8.5 %; specific pore volume of 0.506 cm³/g, and sorption capacity of 0.56 g/g.

The optimum pH value of the solution which is advisable for extracting petroleum products was determined beforehand. The model solutions, containing 100 mg/dm³ of petroleum products with pH = 1.65, 4.01, 6.86, 8.12, 9.18, and 11.34, were prepared. The model solutions with calibrated content were prepared on the basis of the standard sample of the composition of petroleum products solution in carbon tetrachloride by state standard samples 7822-2000 (Russia). The

solutions used for maintaining a certain pH value were prepared on the basis of the standard titers for preparing buffer solutions of operational pH standards of the 3rd class standard captions (SC) SC-pH-04.3 (Russia) in accordance with state industry standard (SIS) SIS 8.135-2004 (Russia). The model solutions in the amount of 1 dm³ were passed through a column filled with the modified sorbent (Figure 1). The quantity of the sorbent for each model solution was fixed at 5.0 g. The inner diameter of the column was 12.5 mm, and the thickness of the sorbent layer was 61.2 mm. The experiments on pH optimization were performed at constant filtration rate $w = const$ with filtrate takeout of 0.1 dm³/min. The content of petroleum products in the filtrate was determined by means of IR spectrometry on the PCM-025 concentration meter.

The efficiency of petroleum products extraction was determined as the ratio of the mass of petroleum products trapped by the sorbent to the weight of petroleum products in the initial

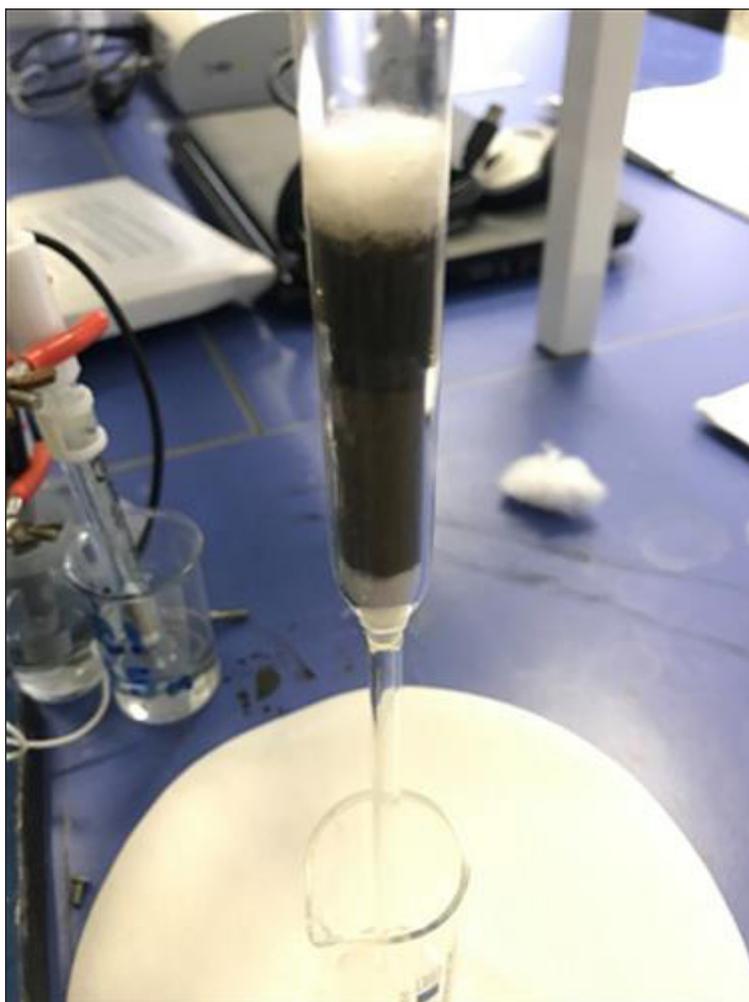


Figure 1. The column filled with the modified sorbent

solution, expressed as a percentage. For this purpose, the following material balance was made:

$$V = V_f + V_s \quad (1)$$

$$VC = V_f C_f + V_s C_s \quad (2)$$

where V was the volume of the initial solution, $V = 1 \text{ dm}^3$ (*const*);

C was the concentration of petroleum products in the initial solution, $C = 100 \text{ mg/dm}^3$ (*const*);

V_f was the volume of the filtrate, dm^3 ;

C_f was the concentration of petroleum products in the filtrate, mg/dm^3 (by concentration meter);

V_s was the pore volume in the sorbent, dm^3 ; and

C_s was the concentration of petroleum products in the sorbent, mg/dm^3 .

The pore volume in the sorbent V_s , dm^3 is determined by multiplying the specific pore volume v , dm^3/g by the weight of the weighed amount of the sorbent m , expressed in g:

$$V_s = vm = 0.506 \cdot 5 / 1000 = 2.53 \cdot 10^{-3} \quad (3)$$

The volume of the filtrate V_f , dm^3 , is found from the overall material balance (1):

$$V_f = V - V_s = 1 - 2.53 \cdot 10^{-3} = 0.99747 \quad (4)$$

From the petroleum products material balance (2), the concentration of petroleum products in the sorbent C_s , mg/dm^3 was determined. The experimental and calculated data are shown in Table 1.

Figure 2 shows the obtained dependence of the efficiency of extracting petroleum products on the pH value of the solution. In the further experimental studies, $\text{pH} = 7.5$ was adopted.

In order to determine the working range of water pollution with petroleum products, a series

of model solutions were prepared, containing the petroleum products in the range between 0.5 and 10 mg/dm^3 with the increment of 0.5, between 10 and 100 mg/dm^3 with the increment of 10, and between 100 and 1,000 mg/dm^3 with the increment of 100. Similarly as in the previous experiment, the quantity of the sorbent for each model solution was fixed at 5.0 g. The model solutions in the amount of 1 dm^3 were passed through a column filled with the modified sorbent at a constant filtration rate $w = \text{const}$ with filtrate takeout of 0.1 dm^3/min . The content of petroleum products in the filtrate was determined by means of IR spectrometry on the PCM-025 concentration meter. The efficiency of petroleum products extraction was determined in a similar way using expressions (1) – (4). The experimental and calculated data are shown in Table 2. The maximum extraction of petroleum products from the solution was 88.23%. Figure 3 shows the dependence of petroleum products extraction efficiency in % on the concentration of petroleum products in the solution C mg/dm^3 , in a logarithmic system of coordinates by abscissa X-axis. While analyzing this dependence, one can draw a conclusion that the sorbent can ensure 85% efficiency of removing the petroleum products from the wastewater in the range of pollution between 5 and 300 mg/dm^3 .

The analysis of the data in Table 2 shows that when the concentration of petroleum products in the solution C increases, the concentration of petroleum products in the sorbent C_s and in the filtrate C_f increases as well. Simultaneously, the ratio of petroleum products concentration in the sorbent to the concentration of petroleum products in the filtrate increases to a certain limit (maximum) value (Figure 4, logarithmic system of coordinates by X-axis), which characterizes the equilibrium between the filtrate and the sorption liquid. The sorption liquid is enclosed in the pores of the sorbent and adsorbed on its surface. Such an experimentally found limit ratio of the

Table 1. Experimental and calculated data of the pH solution optimization

pH	The concentration of petroleum products in the filtrate, mg/dm^3	The concentration of petroleum products in the sorbent, mg/dm^3	The amount of petroleum products in the sorbent, mg	The efficiency of petroleum products extraction, %
1.65	21	31,246.3	79.05	79.05
4.01	19	32,034.8	81.05	81.05
6.86	18	32,429.1	82.05	82.05
8.12	17	32,823.3	83.04	83.04
9.18	18	32,429.1	82.05	82.05
11.34	19	32,034.8	81.05	81.05

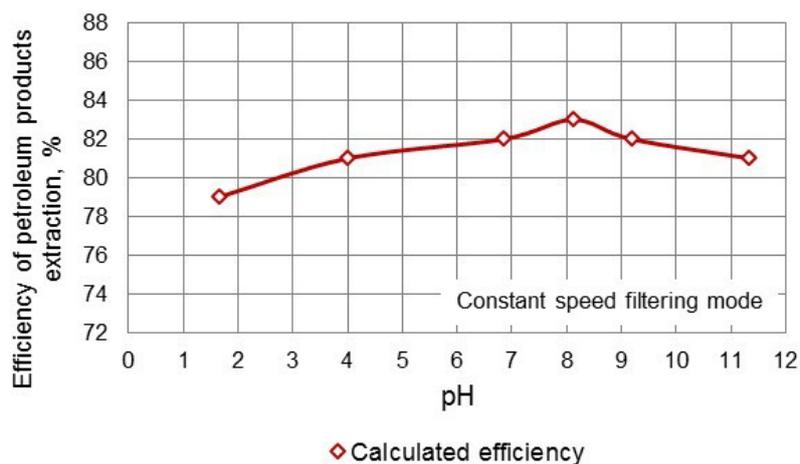


Figure 2. Dependence of the efficiency of extracting petroleum products on the pH value of the solution.

Table 2. Experimental and calculated data for determining the working range of water pollution with petroleum products

Petroleum products concentration in the solution C_s , mg/dm ³	The amount of petroleum products in the solution, mg	Petroleum products concentration in the filtrate C_p , mg/dm ³	Petroleum products concentration in the sorbent C_s' , mg/dm ³	The amount of petroleum products in the sorbent, mg	The efficiency of petroleum products extraction, %	C_s / C_f
0.5	0.5	0.204	117.20	0.296516	59.30	574.51
1	1	0.308	273.83	0.692779	69.28	889.0448
2	2	0.394	635.18	1.606997	80.35	1,612.123
3	3	0.432	1,015.45	2.569093	85.64	2,350.583
4	4	0.488	1,388.63	3.513235	87.83	2,845.554
5	5	0.595	1,741.70	4.406505	88.13	2,927.23
6	6	0.708	2,092.41	5.293791	88.23	2,955.378
7	7	0.826	2,441.14	6.17609	88.23	2,955.378
8	8	0.944	2,789.88	7.058388	88.23	2,955.378
9	9	1.071	3,135.06	7.93171	88.13	2,927.23
10	10	1.19	3,483.40	8.813011	88.13	2,927.23
20	20	2.38	6,966.81	17.62602	88.13	2,927.23
30	30	3.6	10,438.38	26.40911	88.03	2,899.551
40	40	4.8	13,917.84	35.21214	88.03	2,899.551
50	50	6.05	17,377.59	43.96531	87.93	2,872.329
60	60	7.26	20,853.11	52.75837	87.93	2,872.329
70	70	8.54	24,301.03	61.48161	87.83	2,845.554
80	80	9.76	27,772.61	70.26469	87.83	2,845.554
90	90	11.07	31,208.70	78.95801	87.73	2,819.214
100	100	12.4	34,636.91	87.63137	87.63	2,793.299
200	200	25	69,194.96	175.0633	87.53	2,767.798
300	300	43.2	101,545.18	256.9093	85.64	2,350.583
400	400	79.6	126,719.92	320.6014	80.15	1,591.959
500	500	114.5	152,486.04	385.7897	77.16	1,331.756
600	600	172.2	169,263.11	428.2357	71.37	982.9449
700	700	277.2	167,391.82	423.5013	60.50	603.8666
800	800	404.8	156,610.33	396.2241	49.53	386.8832
900	900	591.3	122,607.11	310.196	34.47	207.3518
1000	1000	800	79,851.38	202.024	20.20	99.81423

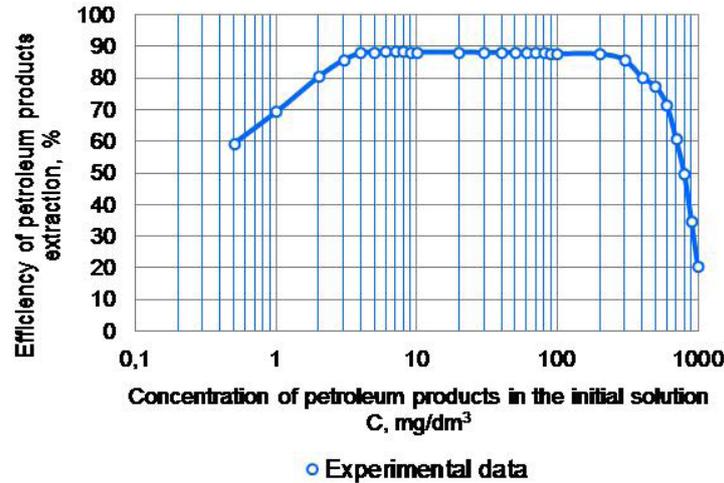


Figure 3. Dependence of the efficiency of petroleum products extraction from the solution on the concentration of petroleum products in the initial solution

concentrations determines the adsorption equilibrium constant. In this case, the adsorption equilibrium constant was 2,955.4.

The analysis of Figure 3 shows that the removal of 85% of petroleum products from the wastewater is achieved in the contamination range between 5 and 300 mg/dm³. With the concentration of petroleum products in the solution $C = 300$ mg/dm³, the concentration of petroleum products in the filtrate is $C_f = 43.2$ mg/dm³ (Table 2). Let us check the applicability of the Henry's law for the range of petroleum products concentrations in the filtrate up to $C_f = 50$ mg/dm³. The Henry's law is a linear dependence in coordinates $C_s^* = f(C_f)$ [Keltsev, 1984].

$$C_s^* = KC_f \tag{5}$$

where N_s^* is the concentration of the adsorbate in the sorbent, the equilibrium concentration of the adsorptive in the filtrate C_f ; and K is the Henry's law constant (the adsorption equilibrium constant).

The adsorbate and the adsorptive are petroleum products. Table 3 shows the equilibrium concentrations of adsorbate and adsorptive calculated from equation (5). The Henry's law constant is $K = 2,955.4$. Figure 5 shows the comparison of the calculated and the experimental data along the X-axis in a logarithmic system of coordinates. A good qualitative and quantitative agreement is shown for a range of petroleum products concentrations in the filtrate up to $C_f = 50$ mg/dm³, which confirms the known data about the applicability of the Henry's law for low concentrations of the adsorptive in the filtrate.

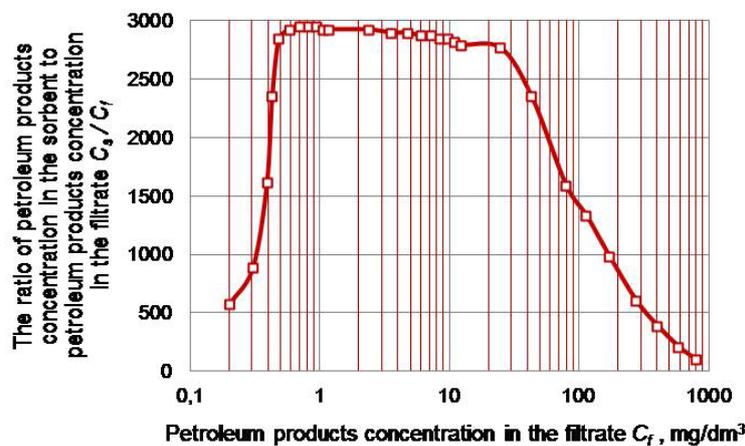


Figure 4. Determination of the adsorption equilibrium constant for dynamic sorption

Table 3. The data calculated by the Henry's law

C_f	C_s^*
0.1	295.54
0.2	591.08
0.5	1,477.7
1	2,955.4
2	5,910.8
3	8,866.2
4	11,821.6
5	14,777
6	17,732.4
7	20,687.8
8	23,643.2
9	26,598.6
10	29,554
20	59,108
30	88,662
40	118,216
50	147,770
60	177,324
70	206,878
80	236,432
90	265,986
100	295,540

In order to assess the effect of the matrix of natural fresh water on the degree of petroleum products extraction, a model solution was prepared with the content of petroleum products of 100 mg/dm³, including the natural compounds, the composition of which is shown in Table 4.

During the experiment, two model solutions of petroleum products in the freshwater matrix were analyzed after the treatment with the modified sorbent for preventing random measurement results. The results of the studies are shown in Table 5.

The analysis of the obtained data showed that the average degree of petroleum products extraction during the experiment was 85.5%. From the data presented above, a conclusion can be drawn that the natural water matrix has an insignificant effect on the sorption of petroleum products.

CONCLUSION

The obtained experimental data show the applicability of the modified sorbent for removing the petroleum products from wastewater

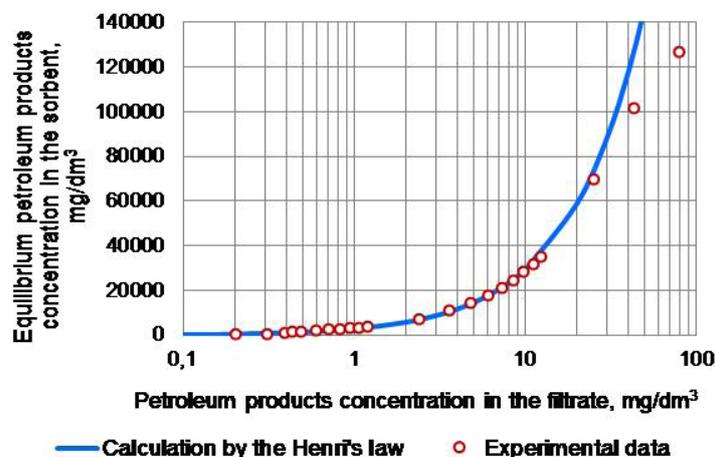


Figure 5. Comparison of the experimental to the calculated data according to the Henry's law

Table 4. Mass content of the main compounds in natural freshwater

Substance	NaHCO ₃	MgSO ₄	K ₂ HPO ₄	KH ₂ PO ₄	(NH ₄) ₂ SO ₄	NaCl	FeSO ₄	NaNO ₃	CaSO ₄
Content, mg/dm ³	10	1	1	1	100	100	10	1	1

Table 5. Determination of petroleum products concentration in model solutions with regard to the natural freshwater matrix

Number of solution	Eluate dilution factor, K	Sample volume, V, dm ³	Eluate volume, B, dm ³	Instrument readings, C, mg/dm ³	The content of petroleum products in the sample, X, mg/dm ³	Expanded uncertainty ±U (with P = 0.95), mg/dm ³
1	10	0.95	0.027	50.2	14.3	3.7
2	10	0.95	0.028	50.0	14.7	3.8

with ensuring the cleaning efficiency of at least 85% in the range of pollution between 5 and 300 mg/dm³. The modified sorbent was obtained from the wastes accumulated at ash dumps using the hydraulic ash disposal method and classified as hazard class V, according to the results of quantitative chemical analysis and biotesting. These wastes are inexpensive and readily-available. The disposal of ASW will result in freeing land, reducing the pressure on the natural environment, and improving the ecological situation in the adjacent urbanized areas.

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