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EVALUATION OF ADSORPTION OF PETROLEUM PRODUCTS IN THE SOIL DEPENDING ON ITS GRANULATION**

1. INTRODUCTION

In the today's world petroleum products are used on a large scale, so the danger of introducing uncontrolled into the environment oil pollution is widespread. In the case of the detection of such situation it is required to take immediate, rational course of action aimed at reducing pollution range, and ultimately at its removal. A necessary condition for this is the ability to predict the scenario of such events, which in turn requires knowledge of the mechanisms of spreading oil pollution in the soil [2, 3].

In the processes that support the migration of petroleum products in the soil the hydrocarbon sorption phenomenon on the solid phase of the soil is especially important. The hydrocarbon adsorption on grains of soil causes a temporary binding of pollution vitally influencing the spatial extent of contamination. The hydrocarbon desorption will result in the release and migration of pollutants for a long time after they had entered in an uncontrolled way to the soil. Therefore the desorption decides in a very important way about the duration of the emergency.

The purpose of this study is to analyze the phenomenon of the hydrocarbon adsorption on a solid phase bulk soils. Five specially selected physical models and a series of sandy soil mixed models were prepared, obtained by mixing the reference soil in a certain proportion. The hydrocarbon adsorption coefficient values were specified as the result of the direct laboratory analysis. In the research there were used typical, commonly utilized motor fuels – unleaded petrol and diesel. Results were precisely analyzed.

Each soil has its own ability of the hydrocarbon adsorption on the mineral skeleton. Usually the attempts to mathematically describe the hydrocarbon migration in the soils with out the knowledge of their sorption properties lead to inaccuracies, which in practice may be

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reflected by poor planning of remediation procedures and further may cause unnecessary costs. In order to quantitatively describe the migration delay of the petroleum contamination in soil volume the delay factor R is introduced, which is equal to the quotient of the average actual velocity of the petroleum contamination movement in the soil to take filtration velocity resulting from the Darcy's law. Adsorption and later desorption of hydrocarbons will result in the appearance of the difference in the values of these velocities. When R = 1 the sorption processes do not occur. For the typical sandy soils the delay factor R varies from few to several, which is generally considered to be a slight delay in a comparison to the soil which contains clay minerals and / or organic matter [4]. However, the comparison of the results of numerical simulation with the real course of the hydrocarbon migration in sandy soils usually indicates the overestimated of the contaminated area and underestimation of the duration of these processes in the calculation. This is due to the fact that in the literature the problem of the hydrocarbon sorption and desorption in the soils doesn't have satisfactory analytical solutions yet. Their development requires detailed quantitative analysis of the soil sorption capacity. This work may be one of the steps of such research [1, 2, 3].

2. SOIL MODELS

In order to carry out the research five reference, specially selected models of sandy soil were prepared, identified with the symbols: M1, M2, M3, M4 and M5 [1]. The distribution of the grains in each model was determined by execution of sieve size analysis, carried out according to the Polish norm. The results are given in the Table 1 and are shown in the Figures 1–5. Selected descriptive statistics and the physical properties of the prepared soil models are presented in the Table 2.

Table 1

The grain size distribution of the prepared sandy soil models

No.	Fraction name in the class	The class limits		The grain size distribution				
				The soil model				
		d_{min}	d_{max}	M1	M2	M3	M4	M5
		mm	mm	%	%	%	%	%
1	*dust*	1/32	1/16	0.000	0.640	0.067	0.000	0.161
2	*sand*	1/16	1/8	0.007	2.229	0.989	0.007	2.785
3	*sand*	1/8	1/4	0.027	9.920	3.857	0.022	22.159
4	*sand*	1/4	1/2	0.308	19.449	93.160	0.055	46.418
5	*sand*	1/2	1	6.424	35.423	1.785	0.070	26.680
6	*sand*	1	2	92.294	23.348	0.074	0.654	1.615
7	*gravel*	2	4	0.925	5.071	0.027	1.269	0.101
8	*gravel*	4	8	0.009	2.514	0.022	64.400	0.054
9	*gravel*	8	16	0.005	1.405	0.019	33.522	0.027
Sum				100.0	100.0	100.0	100.0	100.0

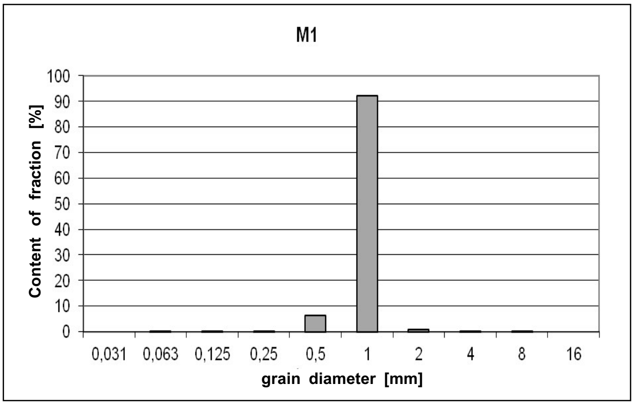

Fig. 1. Distribution histogram of grains in the soil model M1

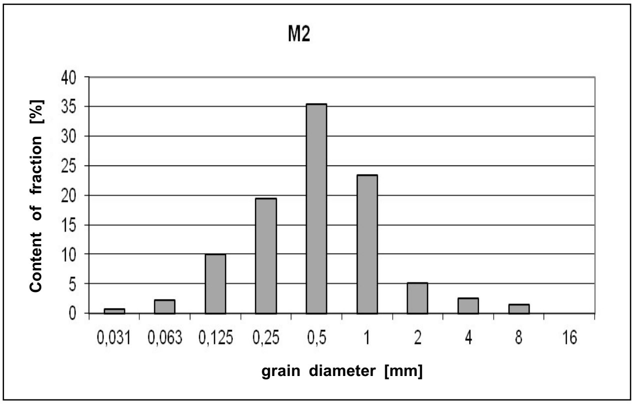

Fig. 2. Distribution histogram of grains in the soil model M2

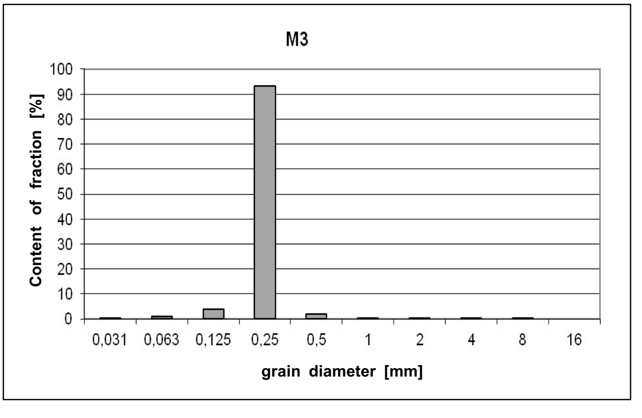

Fig. 3. Distribution histogram of grains in the soil model M3

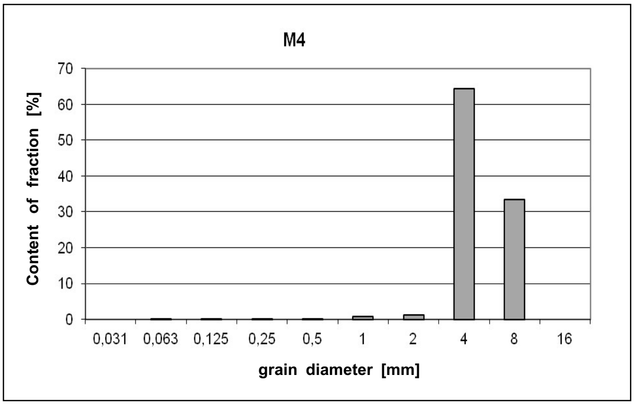

Fig. 4. Distribution histogram of grains in the soil model M4

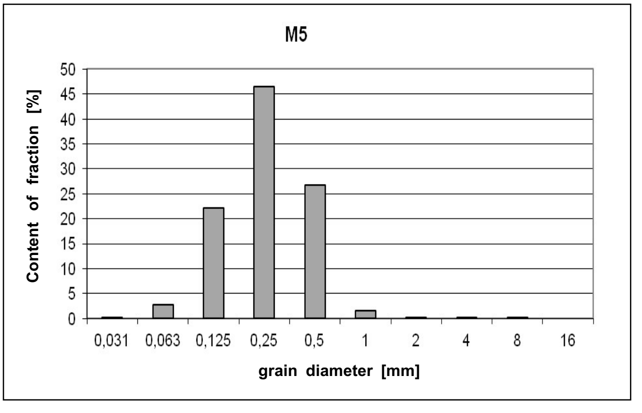

Fig. 5. Distribution histogram of grains in the soil model M5

Table 2

Descriptive statistics and the selected physical properties of the prepared soil models

No.	Parameter	The soil model				
		M1	M2	M3	M4	M5
1	Median d_{50} [mm]	0.685	0.355	0.179	3.397	0.182
2	Effective diameter d_{ef} [mm]	1.244	0.429	0.314	5.997	0.285
3	Heterogeneity factor U [–]	1.44	4.11	1.32	1.71	2.76
4	Discovered porosity n [%]	22.5	21.5	25.0	26.2	15.0
5	Minimum bulk density $\rho_{d.min}$ [kg/m^3]	1490	1430	1450	1490	1520
6	Maximum bulk density $\rho_{d.max}$ [kg/m^3]	1660	1690	1640	1640	1730

In the M1 soil predominates fraction of the grain diameter in the range of 1–2 mm (Tab. 1, Fig. 1). It is more than 92% of the total weight of the mineral skeleton. In addition, it contains a small amount of gravel fractions. On this basis, it can be classified as highly grained sand (PN-R-04033: 1998). It is characterized by the heterogeneity factor equal 1.44, which indicates that it is a homogeneous soil (U < 5). The median is 0.685 mm, and the effective diameter d_{ef} = 1.244 mm (Tab. 2).

In the M2 soil sand fraction predominates, as well the grain diameter is in the range of 0.25 to 2 mm (Tab. 1, Fig. 2). It can be classified as a mixture of medium and highly grained sand (PN-R-04033: 1998). It also contains small amount of dusty fraction and gravel fraction. The heterogeneity factor is quite high 4.11 (Tab. 2), which demonstrates that the soil is much less uniform when compared to the M1, but still homogeneous (the coefficient is close to the threshold heterogeneity U < 5). The median is 0.355 mm, and the effective diameter d_{ef} = 0.429 mm (Tab. 2).

The M3 soil is characterized by a high content of sand fraction with a grain diameter in the range of 0.25 to 0.5 mm (Tab. 1, Fig. 3). It also contains trace amounts of dusty and gravel fractions. It can be classified as medium grained sand (PN-R-04033: 1998). The heterogeneity factor is quite low and amounts to 1.31 which shows that soil is highly homogeneous. The median is 0.179 mm and the effective diameter d_{ef} = 0.314 mm (Tab. 2).

In the M4 soil gravel fraction predominates with the grain size in the range from 4 to 16 mm (Tab. 1, Fig. 4). It can be classified as medium gravel (PN-R-04033: 1998). It is characterized by a low rate of the heterogeneity factor 1.71, which shows that it is a homogeneous soil. The median of the soil is 3.397 mm and the effective diameter d_{ef} = 5.997 mm (Tab. 2).

The M5 soil is characterized by a considerable content of the sand fraction with the grain diameter in the range of 0.125 to 1 mm (Tab. 1, Fig. 5), and can be classified as fine grained sand (PN-R-04 033: 1998). The heterogeneity factor is 2.76 which indicates a homogeneous soil, but sorted out to a smaller extent than the soils M1, M3 and M4. The median is equal to 0.182 mm and the effective diameter d_{ef} = 0.285 mm (Tab. 2).

The soils M1, M3 and M4 which have very low values of the heterogeneity factor indicating high degree of grains sorting were used to prepare the mixed soil, containing in its composition mixed reference soils in a certain proportion. The soils M2 and M5 were natural aggregates used for comparison to verify the results obtained for the artificial mixed models.

3. HYDROCARBON ADSORPTION COEFFICIENT MEASUREMENT

Adsorption coefficient measurements were conducted on a specially prepared position in three independent series, repeated three times for each case study:

- Series I – mixed soil formed by mixing the reference soils M1 and M3 in appropriate proportion.
- Series II – mixed soil formed by mixing the reference soils M1 M3 and M4 in appropriate proportion.
- Series III – the reference soils M2 and M5.

The measurement results are presented in the Tables 3–8.

Table 3

The adsorption measurement results of unleaded petrol in soil for the series I

		The composition of the mixed model								
Reference model	**M3**	**100%**	**90%**	**75%**	**60%**	**50%**	**40%**	**25%**	**10%**	**0%**
	M1	**0%**	**10%**	**25%**	**40%**	**50%**	**60%**	**75%**	**90%**	**100%**
Adsorption coefficient [g/g d.m.]	E_1	0.222	0.196	0.189	0.167	0.143	0.158	0.158	0.132	0.103
	E_2	0.219	0.210	0.177	0.178	0.151	0.143	0.151	0.120	0.113
	E_3	0.211	0.204	0.173	0.170	0.141	0.155	0.139	0.113	0.124
Average	$E_{śr}$	0.217	0.203	0.180	0.172	0.145	0.152	0.150	0.122	0.114
St. Dev.	s	0.0058	0.0073	0.0078	0.0057	0.0051	0.0083	0.0095	0.0096	0.0106
Mean Err.	δ	0.0033	0.0042	0.0045	0.0033	0.0030	0.0048	0.0055	0.0056	0.0061
Sig. Lev.	α	0.0143	0.0181	0.0195	0.0141	0.0127	0.0206	0.0236	0.0239	0.0262

Table 4

The adsorption measurement results of diesel in soil for the series I

		The composition of the mixed model								
Reference model	**M3**	**100%**	**90%**	**75%**	**60%**	**50%**	**40%**	**25%**	**10%**	**0%**
	M1	**0%**	**10%**	**25%**	**40%**	**50%**	**60%**	**75%**	**90%**	**100%**
Adsorption coefficient [g/g d.m.]	O_1	0.202	0.207	0.178	0.169	0.152	0.163	0.144	0.142	0.125
	O_2	0.238	0.188	0.167	0.158	0.156	0.151	0.142	0.134	0.138
	O_3	0.205	0.192	0.163	0.163	0.165	0.152	0.157	0.130	0.125
Average	$O_{śr}$	0.215	0.195	0.170	0.163	0.158	0.155	0.148	0.135	0.130
St. Dev.	s	0.0201	0.0100	0.0076	0.0056	0.0064	0.0068	0.0080	0.0060	0.0072
Mean Err.	δ	0.0116	0.0058	0.0044	0.0032	0.0037	0.0039	0.0046	0.0035	0.0042
Sig. Lev.	α	0.0499	0.0249	0.0189	0.0139	0.0159	0.0169	0.0200	0.0150	0.0180

Table 5

The adsorption measurement results of unleaded petrol in soil for the series II

		The composition of the mixed model						
Reference model	**M4**	**0%**	**0%**	**10%**	**40%**	**70%**	**90%**	**100%**
	M3	**100%**	**0%**	**45%**	**30%**	**15%**	**5%**	**0%**
	M1	**0%**	**100%**	**45%**	**30%**	**15%**	**5%**	**0%**
Gasoline adsorption coefficient on solid phase of soil [g/g d.m.]	E_1	0.222	0.103	0.189	0.143	0.099	0.080	0.053
	E_2	0.219	0.113	0.177	0.130	0.117	0.086	0.060
	E_3	0.211	0.124	0.173	0.132	0.094	0.089	0.060
Average adsorption coeff.	$E_{śr}$	0.217	0.114	0.180	0.135	0.103	0.085	0.058
Standard deviation	s	0.0058	0.0106	0.0078	0.0072	0.0119	0.0046	0.0044
Mean error	δ	0.0033	0.0061	0.0045	0.0041	0.0069	0.0026	0.0025
Mean significance level	α	0.0143	0.0262	0.0195	0.0178	0.0297	0.0114	0.0108

Table 6

The adsorption measurement results of diesel in soil for the series II

		The composition of the mixed model						
Reference model	**M4**	**0%**	**0%**	**10%**	**40%**	**70%**	**90%**	**100%**
	M3	**100%**	**0%**	**45%**	**30%**	**15%**	**5%**	**0%**
	M1	**0%**	**100%**	**45%**	**30%**	**15%**	**5%**	**0%**
Diesel adsorption coefficient on solid phase of soil [g/g d.m.]	O_1	0.202	0.125	0.142	0.137	0.110	0.069	0.050
	O_2	0.238	0.138	0.148	0.149	0.121	0.077	0.059
	O_3	0.205	0.125	0.127	0.144	0.116	0.076	0.054
Average adsorption coeff.	$O_{śr}$	0.215	0.130	0.139	0.143	0.116	0.074	0.054
Standard deviation	s	0.0201	0.0072	0.0108	0.0057	0.0053	0.0042	0.0042
Mean error	δ	0.0116	0.0042	0.0062	0.0033	0.0031	0.0025	0.0024
Mean significance level	α	0.0499	0.0180	0.0268	0.0142	0.0133	0.0105	0.0104

Table 7

The adsorption measurement results of unleaded petrol in soil for the series III

Parameter	**Symbol**	**The soil model**	
		M2	**M5**
Gasoline adsorption coefficient on solid phase of soil [g/g d.m.]	E_1	0.166	0.177
	E_2	0.151	0.173
	E_3	0.185	0.189
Average gasoline adsorption coefficient [g/g d.m.]	$E_{śr}$	0.167	0.180
Standard deviation of measurement results [g/g d.m.]	s	0.0170	0.0078
Average absorption coefficient error [g/g d.m.]	δ	0.0098	0.0045
Significance level of average absorption coefficient	α	0.0422	0.0195

Table 8

The adsorption measurement results of diesel in soil for the series III

Parameter	**Symbol**	**The soil model**	
		M2	**M5**
Diesel adsorption coefficient on solid phase of soil [g/g d.m.]	O_1	0.188	0.188
	O_2	0.180	0.184
	O_3	0.201	0.201
Average diesel adsorption coefficient [g/g d.m.]	$O_{śr}$	0.189	0.191
Standard deviation of measurement results [g/g d.m.]	s	0.0105	0.0087
Average absorption coefficient error [g/g d.m.]	δ	0.0061	0.0050
Significance level of average absorption coefficient	α	0.0261	0.0216

4. RESULTS ANALYSIS

In the first measurement series the hydrocarbon adsorption coefficient was studied on the solid phase mixed soil models obtained by mixing the perfectly sorted reference model of sandy soil M3 – medium sand and M1 – coarse sand in fixed proportion. In total there were nine mixed models prepared. This allowed to densely cover with measurements the range of variation in effective diameter of soil from 0.314 mm to 1.244 mm. For each of the mixed models the measurements of gasoline and diesel oil adsorption coefficient were repeated three times. Partially the repeated hydrocarbon adsorption coefficients significantly different from each other. In the case of unleaded petrol adsorption studies on the mineral skeleton of soil model the standard deviation of the repeated measurements is approximate from 3% of the adsorption coefficient for medium sand mean value to almost 10% of the mean value in the case of coarse sand (Tab. 3). The results related to the adsorption of diesel on the mineral skeleton of soil model the standard deviation of the repeated measurements is approximately 5% to almost 10% of the adsorption coefficient average value (Tab. 4). In general, the dispersion results of the repeated measurements increases with the increase of the effective grains diameter of soil model. This phenomenon can be explained by the fact that the hydrocarbon filtration velocity increase with the increase of the soil grains diameter (as a consequence of the increase of the cross-section of pores), which leads to incomplete wetting of the mineral skeleton soil model by hydrocarbons (if filtration is not the entire volume of the pore space of the soil) [2, 4] . This thesis confirms the much higher dispersion of the repeated measurements at relatively large values of the effective diameter compared to diesel fuel which has a several times higher viscosity. Despite the scatter of the repeated measurements in the first series for each of the 18 cases considered, the significance level of the average coefficient of hydrocarbon adsorption is less than usually adopted in this case, $\alpha = 0.05$, therefore, the calculated average values of the adsorption coefficient should be considered as significant (Tabs 3 and 4). The calculated level of precision the adsorption coefficient average value for unleaded petrol varies in the range from 1.27% to 2.62%. The diesel situation is slightly worse, because in one of the cases the significance level reaches $\alpha = 4.99\%$.

In the second measurement series the hydrocarbon adsorption coefficient was studied on the solid phase mixed soil models obtained by mixing the perfectly sorted reference model of sandy soil M3 – medium sand, M1 – coarse sand and M4 – gravel in fixed ratio. In total seven mixed models were prepared. This allowed to cover evenly with measurements the range of the effective soil diameter changes from 0.314 mm to 5.997 mm. For the each of the mixed model the measurements of gasoline and diesel oil adsorption coefficient were repeated three times. Similarly to the first series the partial repeated measurements of the hydrocarbon adsorption coefficient significantly differs from each other. In the case of unleaded petrol adsorption studies on the mineral skeleton of soil model the standard deviation of the repeated measurements is approximate from 3% of the adsorption coefficient for medium sand mean value to almost 12% of the mean value in the case of the one of the mixed models (Tab. 5). In the case of the diesel adsorption studies on the mineral skeleton of soil model the standard deviation of the repeated measurements is from 6% to nearly 10% of the adsorption coefficient average value (Tab. 6). In general, dispersion of the results of the repeated measurements increases with the increase of the effective grains diameter in the soil model. This phenomenon can be explained, as previously, by the fact that the hydrocarbon filtration velocity increases with the increase of soil grains diameter, which leads to incomplete wetting of the mineral skeleton soil model by hydrocarbons (the filtration then does not use the entire volume of the pore space of soil) [2, 4]. However, this does not explain all of the observed discrepancies. It seems that it is due to the inaccurate mixing of the mixed model ingredients – medium sand, coarse and gravel [2]. Despite the scatter of the repeated measurements at the second series, for each of the 14 cases considered the significance level for the average coefficient of hydrocarbon adsorption is less than usually adopted in such case, $\alpha = 0.05$, therefore, the calculated average adsorption coefficient is considered to be significant (Tabs 5 and 6). The calculated level of precision of the adsorption coefficient average value for unleaded petrol changes in the range from 1.14% to 2.97%. The diesel situation is slightly worse, because in the one of the case the significance level reaches $\alpha = 4.99\%$.

In the third measurement series only two reference soil models were examined: M2 and M5 with the lowest degree of sorting. In this case, the results of the repeated measurements are slightly different from each other as well. For unleaded petrol the standard deviation of the hydrocarbon adsorption coefficient on mineral skeleton is from 5% to almost 11% of its average value (Tab. 7). The calculated mean values of the adsorption coefficient of unleaded petrol are significant at the significance level of at least $\alpha = 4.22\%$. For diesel the standard deviation of the hydrocarbon adsorption coefficient on mineral skeleton is from 6% to about 8% of its mean value (Tab. 8). The calculated mean values of the adsorption coefficient of diesel are significant at the significance level of at least $\alpha = 2.61\%$.

5. CONCLUSIONS

As a result of the studies of the adsorption coefficient of unleaded petrol and diesel on mineral skeleton for prepared models of sandy soil the following was stated:

1. The increase in scatter of the repeated partial measurements of hydrocarbon adsorption with an increase in effective diameter, which is explained by the higher velocity of oil products filtration in the ground and incomplete wetting of its mineral skeleton. The number of soil grains remaining without contact with the hydrocarbons in a given situation is random and depends on their mixing.
2. The increase in spread of the repeated partial measurements of hydrocarbon adsorption for soil mixed with different granulometric composition, which explains the unrepeatability and the lock of uniformity in mixing.
3. The hydrocarbon adsorption coefficient on solid phase of soil strongly decreases with the increase of effective grains diameter.
4. The calculated values of the average hydrocarbon adsorption coefficient from the repeated measurements are highly significant from a statistical point of view and have a representative character. They can be used in the future while trying to develop a model describing the changes in the hydrocarbon adsorption coefficient values as a function of the effective grains diameter with a better result than using only direct partial findings.

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