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MAGNITUDE OF HYDROCARBON SORPTION CAPACITY OF SANDY SOILS ANALYSIS**

1. INTRODUCTION

Cases of environmental pollution caused by oil and petroleum products commonly occur nowadays. Leaving the hydrocarbon contamination in soil and aquatic environments is usually not an option, because they create too big threat to life and health of animals and humans [4]. In the event of such an incident or detection of such a situation it is required to take immediate action to reduce pollution range and then to ultimately remove it. Planning the scenario of properly conducted course of action requires the skill to predict the petroleum migration processes in the soil, which is not possible without the knowledge of its mechanism [2, 3].

One of the key processes accompanying migration of petroleum contaminants in soil are the sorption processes occurring on the surface of the sandy soil grains [3]. Adsorption of hydrocarbons causes the temporary immobilisation, thereby reduces the range of penetration of oil pollution. Desorption causes the hydrocarbons release at a later time, which increases the migration process. The knowledge of the soil sorption capacity for the oil products is therefore necessary to plan actions to stop and remediate of contamination and environment cleaning. This work may help to assess the quantity of hydrocarbons temporary accumulated in the sandy soil.

2. SCOPE OF THE RESEARCH

During the previous studies the adsorption of hydrocarbons coefficient has been measured. The studies were conducted on mineral skeleton of especially prepared models of

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sandy soil. The research was carried out commonly used petroleum substances, namely motor fuel – unleaded petrol and diesel fuel. The measurement was realized in three series [1]:

1. Series I – there were nine different models of sandy soil prepared; 27 independent measurements of the adsorption of unleaded petrol coefficient (three for each soil model) carried out; 27 independent measurements of the adsorption of diesel fuel coefficient (three for each soil model) made.
2. Series II – there were seven different models of sandy soil prepared; 21 independent measurements of the adsorption of unleaded petrol coefficient (three for each soil model) carried out; 21 independent measurements of the adsorption of diesel fuel coefficient (three for each soil model) made.
3. Series III – there were two different models of sandy soil prepared; 6 independent measurements of the adsorption of unleaded petrol coefficient (three for each soil model) carried out; 6 independent measurements of the adsorption of diesel fuel coefficient (three for each soil model) made.

The results of the three times repeated measurements of hydrocarbon adsorption for the soil model and oil products were characterized by a relatively large scatter [1], which was the reason of:

- Inaccuracy of the measurement method.
- Problems with keeping reproducible conditions of the hydrocarbons filtration:
  - The scatter partial results of repeated measurements increases with the rise of the effective diameter soil model, which may indicate hydrocarbon filtration incomplete pore space of soil, as a consequence of incomplete wetting by hydrocarbon grains of mineral skeleton.
  - The scatter partial results of repeated measurements grows as more diverse granulometric soil model, which may indicate their inaccurate mixing.

In fact, because of too high dispersion the results of repeated partial measurements in five cases (in 36 of all cases) it was decided to take an additional four repeated measurement of the adsorption of hydrocarbons coefficient for a given soil model and oil products. From the four values held the most deviated were rejected.

Conducted attempts to make a correlation and regression analysis the partial absorption of hydrocarbons coefficients depending on the soil granulometric model did not produce satisfactory results, therefore it was decided to limit the dispersion of hydrocarbon partial adsorption coefficients by replacing them with the mean values [1]. The statistical analysis showed that each of the calculated averages is significant and has the representative character.

3. CORRELATION ANALYSIS

In the first step of analysis the correlation of the measured averaged adsorption of hydrocarbons coefficients was performed in a graphical overview for petroleum substances tested in each measuring series on the effective diameter of grains of the soil model (Figs 1–6). Prepared combinations show that there is a very clear trend of the adsorption coefficient of gasoline and diesel on the effective diameter of grains of soil model, which is generally not dependent on the analyzed series of measurements and has the universal character. The results of non-linear regression analysis are shown in the Table 1 and in the Figures 1–6. In every case, the best compatibility of the experimental data with the calculated results was obtained for the power model.

Table 1

Results of non-linear regression analysis of the adsorption of hydrocarbons coefficient on the mineral skeleton and an effective diameter of grains of soil model

The measuring Series	Unleaded petrol	Diesel fuel
Series I		
Form of the equation	$E_{sr} = 0{,}1208 \cdot d_{ef}^{-0{,}449}$	$O_{sr} = 0{,}1326 \cdot d_{ef}^{-0{,}324}$
The determination coefficient R^2	0,9496	0,8793
Series II		
Form of the equation	$E_{sr} = 0{,}1282 \cdot d_{ef}^{-0{,}447}$	$O_{sr} = 0{,}1253 \cdot d_{ef}^{-0{,}448}$
The determination coefficient R^2	0,9860	0,9564
Series III		
Form of the equation	$E_{sr} = 0{,}1438 \cdot d_{ef}^{-0{,}177}$	$O_{sr} = 0{,}1866 \cdot d_{ef}^{-0{,}018}$
The determination coefficient R^2	1,0	1,0

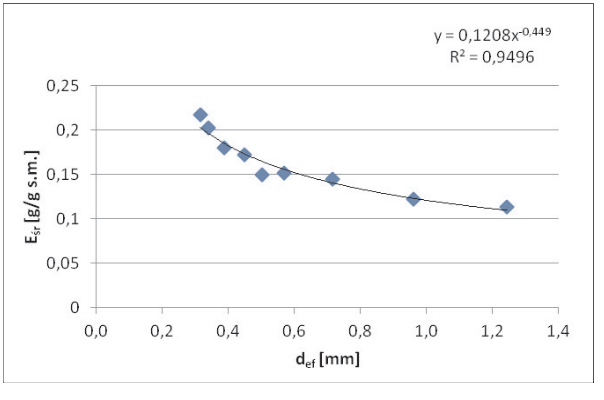

Fig. 1. Averaged gasoline adsorption coefficient in soil for the first series of measurements

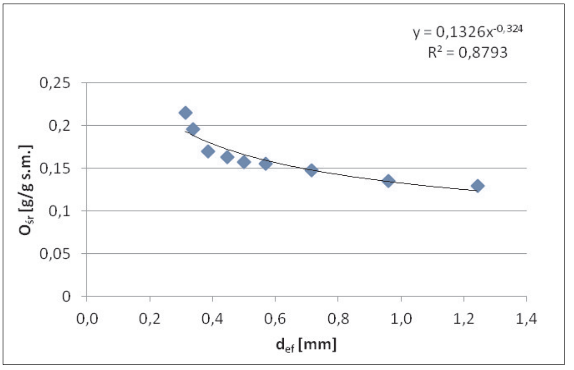

Fig. 2. Averaged diesel adsorption coefficient in soil for the first series of measurements

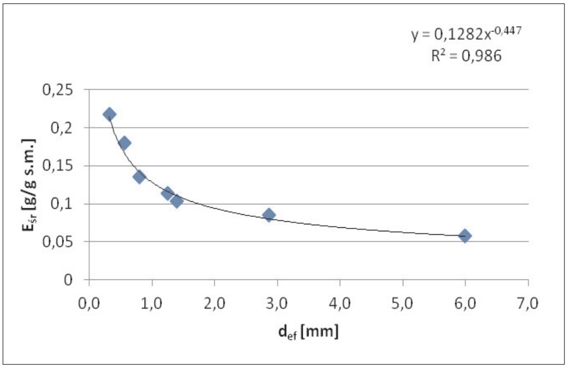

Fig. 3. Averaged gasoline adsorption coefficient in soil for the second series of measurements

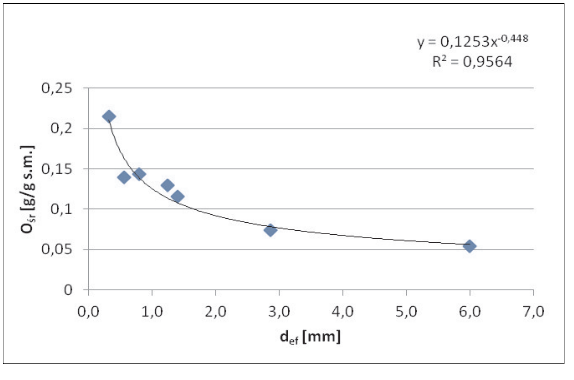

Fig. 4. Averaged diesel adsorption coefficient in soil for the second series of measurements

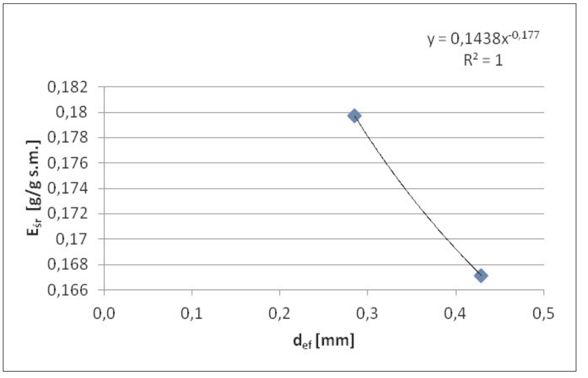

Fig. 5. Averaged gasoline adsorption coefficient in soil for the third series of measurements

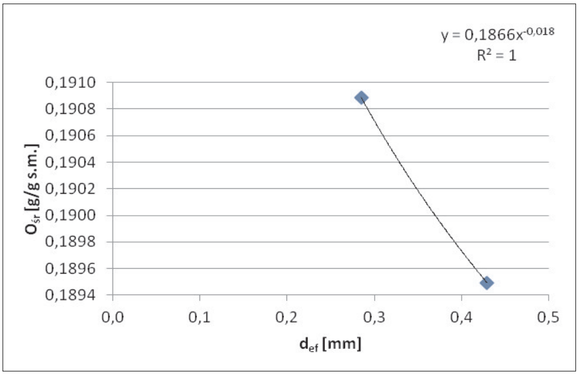

Fig. 6. Averaged diesel adsorption coefficient in soil for the third series of measurements

The form of matching regression depending on the adsorption of unleaded petrol coefficient in the first and the second run is very close – the coefficient in the equation and the power of the independent variable differ only on the third significant digit position. The determination coefficient reaches a very high value from nearly 0.95 to over 0.98. Matching equations describe at least 95% of parameter variability.

In the case of diesel fuel the differences in the form of the fitted regression equations are more clear – the coefficient in the equation differs on the second significant digit position, and the power on the first significant digit position. However, for the first series of measurements the compatibility of the regression equation describes a 88% of parameter variability, and the second run more than 95% of parameter variability.

For the third series of measurements the equation has been matched to two points, and therefore they do not have a representative character.

In the next step of the correlation analysis the results obtained in the each measurement series are presented on one drawing (with distinction between a series of measurements) depending on absorption coefficient for gasoline and diesel on the effective diameter of grains of the soil model (Figs 7–8).

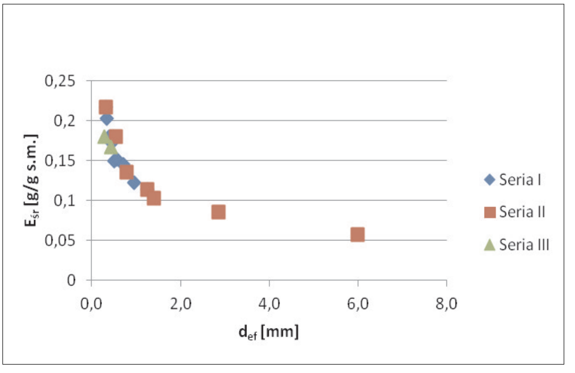

Fig. 7. Averaged gasoline adsorption coefficient in soil for all measurement series

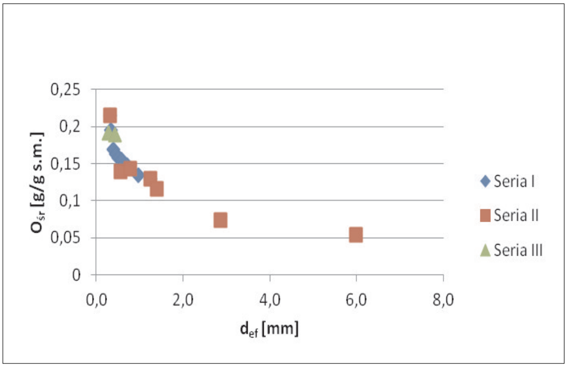

Fig. 8. Averaged diesel adsorption coefficient in soil for all measurement series

In Figures 9–10, the same combination was prepared without distinction between measurement series and the nonlinear regression analysis was performed to fit the form of the trend line to the power model.

Correlation combinations placed in the Figures 7 and 8 show that the results obtained for the different measurement series are arranged along the same trend line. This shows the universal dominant dependence on the adsorption coefficient (sorption capacity) of hydrocarbons on the mineral skeleton of sandy soil and the effective diameter of the grains. The manner of the preparation of a soil model and its extraction do not have a significant effect on the value of the sorption capacity.

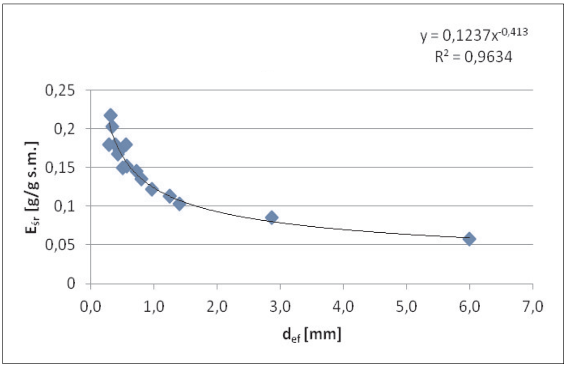

Fig. 9. Matched regression model of changes of the adsorption coefficient of unleaded petrol in soil as a function of effective diameter of grains

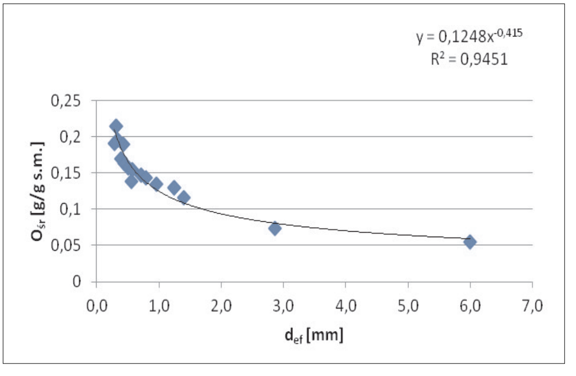

Fig. 10. Matched regression model of changes of the adsorption coefficient of diesel fuel in soil as a function of effective diameter of grains

The Figures 9 and 10 show the results from different measurement series for unleaded petrol and diesel and non-linear regression model fitted to power relationship:

- Dependence of the adsorption of gasoline coefficient on mineral skeleton of sandy soil and the effective diameter of the grains: $E_{sr} = 0{,}1237 \cdot d_{ef}^{-0{,}413}$, coefficient of determination $R^2 = 0{,}9634$,
- Dependence of the adsorption of diesel coefficient on mineral skeleton of sandy soil and the effective diameter of the grains: $O_{sr} = 0{,}1248 \cdot d_{ef}^{-0{,}415}$, coefficient of determination $R^2 = 0{,}9451$.

The forms of regression equation for gasoline and diesel are very similar – the coefficients and the powers differ only on the third significant position. In general, the measured values of the adsorption of unleaded petrol and diesel coefficient in an identical soil model are not very different from each other [1]. The fitting of regression equations to the experimental data is very good. The determination coefficient of the regression equation for unleaded petrol is more than 0.96 (the equation describes more than 96% of parameter variability), whereas for diesel it is than 0.94 (the equation describes more than 94% of the variation of parameters).

4. REGRESSION ANALYSIS

The last step of the conducted studies is the regression analysis. In order to bring the dependence of the hydrocarbon adsorption coefficient on the effective diameter of grains of the soil model to the linear form the log values of both parameters were calculated. On the correlation charts of the Figures 11 and 12 it is shown that the measurement points in this case are arranged along straight lines. The results of linear regression analysis are provided in the Table 2.

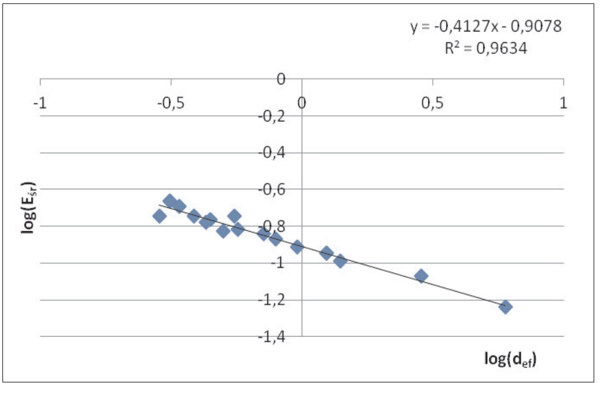

Fig. 11. Matched linear regression model of changes of the adsorption coefficient of unleaded petrol in soil as a function of effective diameter of grains

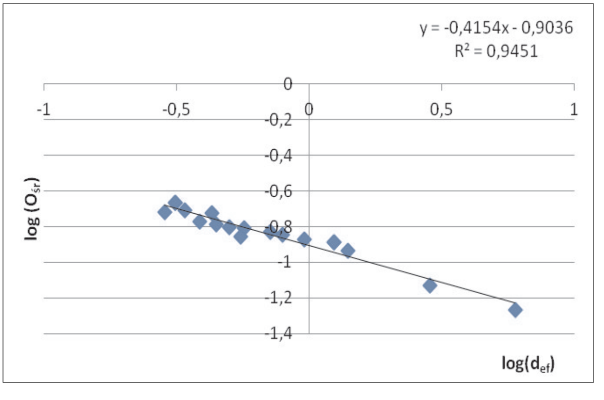

Fig. 12. Matched linear regression model of changes of the adsorption coefficient of diesel fuel in soil as a function of effective diameter of grains

Table 2

The results of linear regression during the analysis of the dependence on the adsorption coefficient of hydrocarbons in sandy soils and the effective diameter of the grains

Characteristics regression dependence	Unleaded petrol	Diesel fuel
The correlation coefficient *R*	0,9816	0,9722
The determination coefficient R^2	0,9634	0,9451
The adjusted determination coefficient R^2	0,9612	0,9417
The standard error of estimate S_e	0,0296	0,0368
The number of observations	18	18
The value of test F Fischer-Snedecor	421,667	275,591
The test F significance	6,4E-13	1,7E-11
The intercept of the regression equation *b*	–0,9078	–0,9036
The standard error of intercept *b*	0,0076	0,0094
The value of statistic t-Student for coefficient *b*	–119,926	–95,874
The significance level of coefficient *b*	4,6E-25	1,6E-23
The lower value of coefficient *b* for 95% confidence interval	–0,9238	–0,9236
The upper value of coefficient *b* for 95% confidence interval	–0,8917	–0,8836
The directional coefficient of the regression equation *a*	–0,4127	–0,4154
The standard error of directional coefficient *a*	0,0201	0,0250
The value of statistic t-Student for coefficient *a*	–20,534	–16,601
The significance level of coefficient *a*	6,4E-13	1,7E-11
The lower value of coefficient *a* for 95% confidence interval	–0,4553	–0,4684
The upper value of coefficient *a* for 95% confidence interval	–0,3701	–0,3623

Both regression equations were calculated by the method of the least squares with a population of 18 attempts. The residual standard deviation called the standard error of estimation of the hydrocarbon adsorption coefficient in the soil for unleaded petrol is 0.0296 and is 0.0368 for diesel fuel. The average size of the empirical values deviations of the hydrocarbon adsorption coefficient from the calculated values with using the regression model is therefore relatively small and indicates a high degree of compatibility of the model to the empirical data. As a result of the regression analysis, the following forms of equations were obtained:

- For unleaded petrol: $\log(E_{sr}) = -0,9078 - 0,4127 \cdot \log(d_{ef})$,
- For diesel fuel: $\log(O_{sr}) = -0,9036 - 0,4154 \cdot \log(d_{ef})$.

The estimated error of the intercept *b* of the regression equation for unleaded petrol is less than 1% of its value, while for diesel is about 1% of its value. This means that the value of the intercept of the regression equation is at least 100 times greater than the error. Based on the Student's t-test it was found that the coefficient *b* is significant at the significance level $\alpha = 4.6 \cdot 10^{-25}$ for unleaded petrol and $\alpha = 1.6 \cdot 10^{-23}$ for diesel, which is much higher than the standard accepted level of 0.05. It follows that the intercepts in both regression equations are very important.

In the obtained equation estimation error of the directional coefficient *a* of the regression equation is 4.87% of its value in the case of unleaded petrol and is 6.01% of its value in the case of diesel. This means that the value of the directional coefficient is more than 20 times greater than the error for unleaded petrol and more than 16 times greater than the error for diesel. Based on the Student's t-test it was found that the coefficient *a* is significant at the significance level $\alpha = 6.4 \cdot 10^{-13}$ for unleaded petrol and $\alpha = 1.7 \cdot 10^{-11}$ for diesel, which is much higher than the standard accepted level of 0.05.

On the basis of the global F-test Fisher-Snedecor the importance of the regression equations on the same significant level was verified, well above the standard accepted level of 0.05. The obtained regression relationship is characterized by a very high regression coefficient $R = 0.9816$ for unleaded petrol and $R = 0.9722$ for diesel, which corresponds with coefficients of determination $R^2 = 0.9634$ and $R^2 = 0.9451$, and means that the obtained regression model explains over 96% of the parameter variability for unleaded petrol and more than 94% of the parameter variation for diesel. Due to the limited sample size corrected coefficients of determination were calculated, but whose values are similar to the coefficients not adjusted.

5. CONCLUSIONS

As a result of the correlation and regression analysis, it was found that:

1. There is a strong correlation between the values of the adsorption coefficient of gasoline and diesel (sorption capacity) and the effective diameter of the grains of sandy soil model.
2. The extraction of the soil model nor the way of its preparation does not significantly affect the relationship referred to in the point 1.
3. The dependence listed in the point 1 has a dominant and universal character.
4. The hydrocarbon adsorption coefficient decreases with the increase of the effective diameter of grains in the soil model according to the power function.
5. Matching regression equations after taking the logarithm of the hydrocarbon adsorption coefficient and the effective diameter of grains (the dependence brought to the linear form) is characterized by a very high compatibility with experimental data – they describe about 95% of parameter variability.
6. The regression equations obtained for gasoline and diesel are very similar to each other, which indicates that the sorption capacity of sandy soil for the both petroleum substances is very close.

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