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EFFECT OF CLAY FRACTION IN SOIL ON BIOAVAILABILITY AND MOBILITY OF DIESEL OIL – MODEL STUDIES

Summary

Contamination of arable lands with hydrocarbon compounds considerably reduces the efficiency and profitability of agricultural production as well as poses a risk of xenobiotics migration into the soil. Therefore, in-depth analyses of biological and physico-chemical phenomena occurring in contaminated soils for the effective prevention of land degradation are crucial. The aim of this study was to evaluate the effect of clay fraction on the bioavailability and mobility of diesel oil in model systems. The results indicate that the clay fraction significantly reduces the mobility of diesel fuel and its toxicity. On the other hand minerals with high sorption properties also reduce quantity of bioavailable hydrocarbons and consequently decrease biodegradation efficiency. Complete remediation of soils with high sorption properties may thus require the use of additional surfactants.
***Key words**: clay fraction, bioavailability, immobilization, diesel oil*

WPŁYW FRAKCJI ILASTEJ GLEB NA BIODOSTĘPNOŚĆ I MOBILNOŚĆ OLEJU NAPĘDOWEGO – BADANIA MODELOWE

Streszczenie

Skażenie gruntów ornych związkami węglowodorowymi w znacznym stopniu ogranicza wydajność i opłacalność produkcji rolniczej a także stwarza ryzyko migracji ksenobiotyków w głąb profilu glebowego. Niezwykle istotna jest zatem dogłębna analiza zjawisk biologicznych i fizykochemicznych zachodzących w zanieczyszczonych glebach celem efektywnego przeciwdziałania degradacji gruntów. Celem niniejszych badań była ocena wpływu frakcji ilastej na biodostępność i mobilność oleju napędowego w układach modelowych. Wyniki wskazują, iż frakcja ilasta w znaczącym stopniu zmniejsza mobilność oleju napędowego i ogranicza jego toksyczność. Z drugiej strony minerały o wysokich właściwościach sorpcyjnych zmniejszają także pulę biodostępnych węglowodorów i w konsekwencji zmniejsza wydajność biodegradacji. Pełna remediacja gleb o wysokich właściwościach sorpcyjnych wymagać może zatem stosowania dodatkowych środków powierzchniowo czynnych.
Słowa kluczowe: frakcja ilasta, biodostępność, immobilizacja, olej napędowy

1. Introduction

Efficiency and profitability of agricultural production is associated with environmental resources of soil - access to water, air and nutrients [7]. The progressive urbanization and mechanization in the agricultural industry result in increasing risk of contamination of agricultural land with hydrocarbon compounds [6]. Frequent spills of petroleum products have a negative effect on the soil fertility [7]. The problem of vertical migration of hydrocarbons into the soil profile, where they can undergo deposition into groundwater should also be considered [10]. The content of the clay fraction possessing high sorption properties is the key factor determining the rate of migration of petroleum compounds. Clay minerals are defined as hydrated silicates of aluminum, iron and magnesium. Depending on the mutual arrangement of the tetrahedral and octahedral, their structure may be bilayer (1: 1) and three-layer (2: 1) [3]. Figure 1. shows a diagram of the crystal lattice of minerals from the kaolinite group.

A significant part of hydrocarbon xenobiotics has the ability to bind to a clay fraction, due to its specific properties such as high cation exchange capacity and a high surface of structure [2]. It is estimated that the surface area of the clay fraction on 1 ha of typical dust soil is up to 25 times larger than the whole area of Poland.

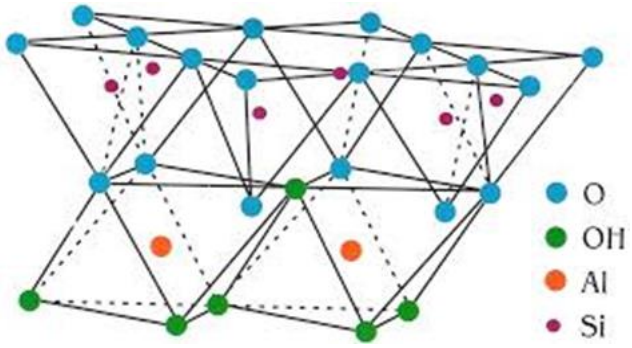

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Fig. 1. Spatial structure of the crystal lattice of minerals from the kaolinite group
Rys. 1. Schemat struktury przestrzennej sieci krystalicznej minerałów z grupy kaolinitu

It should be noted that the process of immobilization of pollutants affect both on the mobility and bioavailability of xenobiotics. Adsorption of hydrophobic pollutants on the surface of mineral particles and within micropores significantly reduces the bioavailability - and consequently the effectiveness of the controlled bioremediation. On the other

hand, clay minerals can significantly reduce the toxicity and thus increase the biodegradation potential of the indigenous microflora to remove xenobiotics. In addition, studies indicate that the sizes of the crystal lattice of clay minerals are similar to the microbial cells, which may mitigate formation of biofilm [1]. The phenomenon of biofilm formation was illustrated by Chaerun et al. [5]. Authors confirmed the ability of microorganisms of the genus Pseudomonas to form biofilm and proliferation on clay minerals (kaolinite and montmorillonite) in the presence of high concentrations of diesel oil (fig. 2).

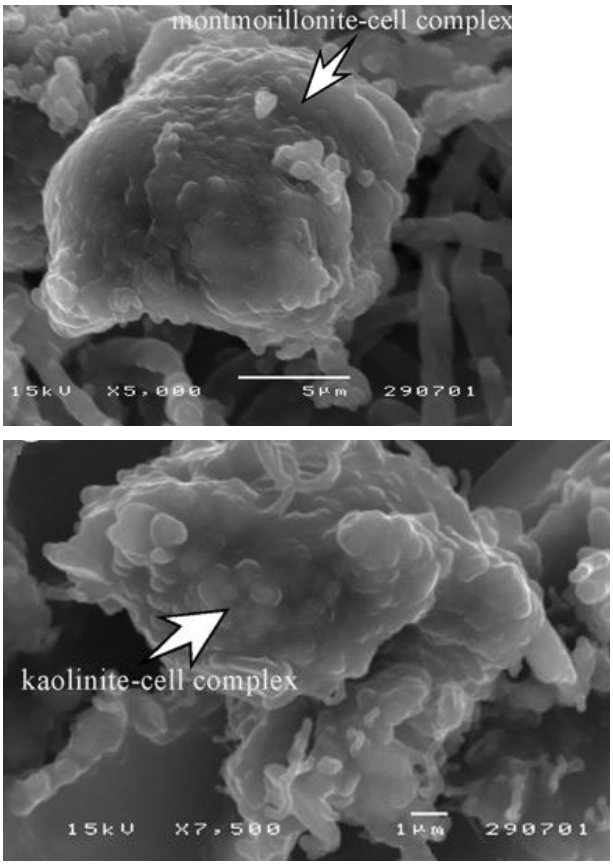

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Fig. 2. Biofilm formation by *Pseudomonas sp*. on the surface of clay minerals - image from a scanning electron microscope
Rys. 2. Tworzenie biofilmu przez Pseudumonas sp. na powierzchni minerałów ilastych – obraz z elektronowego mikroskopu skaningowego

The ability of microbial consortia to form biofilm increases their resistance to environmental stress. It can be therefore believed that microorganisms present in these formations have greater potential for biodegradation and remediation of contaminated soil. The main aim of this research was to assess the impact of the clay fraction on the bioavailability and mobility of diesel oil in model systems.

2. Material and methods

2.1. Microorganisms

Microbial consortium S15 was isolated from soil permanently contaminated with creosote from the area of Solec Kujawski (Poland) (53°04'37.3"N 18°14'44.8"E). Creosote as a treatment for wood preservation (mainly for railways sleepers) was used there for over 100 years up to 2001.

2.2. Chemical reagents

Three commercially available clay minerals (bentonite, kaolinite, and montmorillonite, Sigma-Aldrich, Germany) and mineral medium (MSM) described earlier by Staninska et al. [11] were used. Diesel fuel was purchased at the PKN Orlen station (Poland).

2.3. Determination of the diesel oil sorption on clay minerals

Comparison of sorption properties

Preliminary comparison of the sorption properties of three mineral sorbents was made by the gravimetric test based on the method ASTM F726 99 [8]. The mineral with the best properties were subjected to further analysis.

Determination of the sorption kinetics using Freundlich and Langmuir models

In order to adsorption kinetics modeling, two models: Freundlich (1) and Langmuir (2) were used.

$$C_s = K_f \cdot C_W^{\frac{1}{n}}, \quad (1)$$

where:
C_s – the amount of adsorbate on the adsorbent unit [mg/g],
C_w – the amount of adsorbate in solution after equilibration [mg/l],
K_f –Freundlich constant, – Freundlich exponent.

$$C_s = \frac{K_l \cdot C_w}{1 + b \cdot C_w}, \quad (2)$$

where:
C_s – amount of adsorbate per unit of weight of adsorbent [mg g^{-1}],
C_w – concentration of adsorbate in solution at equilibrium after the adsorption is complete [mg L^{-1}],
K_l – amount of solute adsorbed/unit of weight of an adsorbent in forming a complete monolayer on the surface [mg g^{-1}],
b – constant related to the energy or net enthalpy of adsorption.

The experiment was performed in a model system using a Pyrex glass bottles containing 0.5; 1.0; 2.5; 5.0 and 10 ml of diesel oil with the addition of distilled water to a total volume of 50 ml and 0.5 g of mineral sorbent. Additionally, the series of internal references containing 1 ml and 49 ml of distilled water were studied to determine the possible auto-degradation or volatilization of DO. After two hours of incubation, the concentration of diesel oil in the aqueous phase was determined using a GC-MS chromatography (Shimadzu GC-17A coupled to a mass spectrometer MS-QP5000 with a capillary column Restek RXI-5ms).

2.4. Determination of the diesel oil biodegradation kinetics

Evaluation of the kinetics of biodegradation was carried out in model systems containing 49 ml of MSM, 1 ml of diesel oil, 0.2 g of mineral sorbent and 300µl of microbial inoculate in logarithmic growth phase. Biodegradation lasted 10 days under aerobic conditions with continuous shaking (120 rpm).

3. Results and discussion

Comparison of the sorption of diesel oil on the surface of three used clay minerals is shown in Table 1.

Table 1. Sorption of diesel oil by studied clay minerals
Tab. 1. Sorpcja oleju napędowego dla wybranych minerałów ilastych

Clay mineral	The average amount of diesel oil adsorbed on 1 g of sorbent [g]	Standard deviation [g]
Bentonite	0.71	0.12
Kaolinite	0.59	0.09
Montmorillonite	1.28	0.15

Source: own work / Źródło: opracowanie własne

The highest absorption capacity, defined as the amount of adsorbed diesel oil per 1 g of the sorbent showed montmorillonite and thus it was chosen for further studies of sorption kinetics. The highest sorption properties of this mineral are probably associated with its crystal structures (2:1 type). In this case, the interlayer space has the ability to expand significantly allowing for adsorption inside the structure. On the other hand, kaolinite and bentonite are characterized by 1: 1 construction. The individual packages are permanently linked by hydrogen bonds which determine the low ductility of the interlayers. Therefore, the surface of sorption is limited to the outside crystal structure which determines the lower sorption properties [3]. It should be noted that all of the tested minerals are characterized by sorption ability of diesel oil indicating that soil rich in clay fraction has greater ability to immobilize petroleum hydrocarbons and thus the risk of migration into the soil is relatively low.

Figure 3 shows the Freundlich isotherm, and Figure 4 shows the Langmuir isotherm. In order to determine the proper model, the comparison of correlation coefficient R was performed.

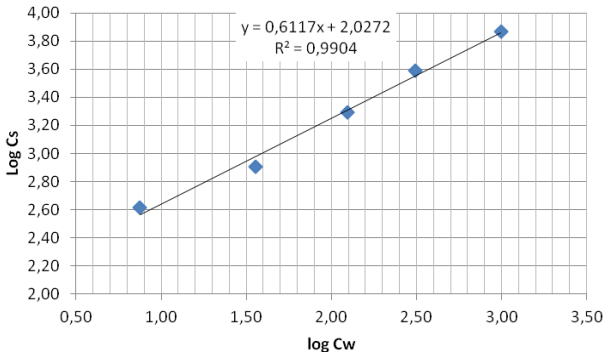

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Fig. 3. Freundlich isotherm for diesel oil on montmorinollite
Rys. 3. Izoterma Freundlicha sorpcji oleju napędowego na strukturze montmorylonitu

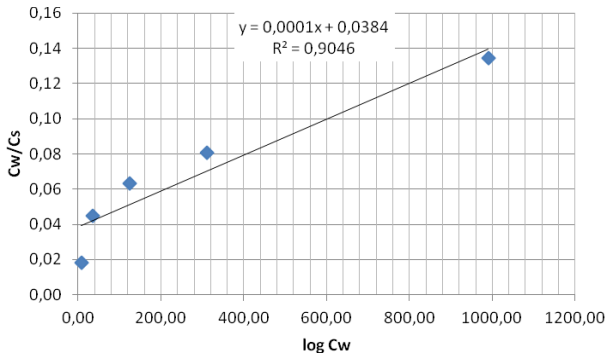

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Fig. 4. Langmuir isotherm for diesel oil on montmorinollite
Rys. 4. Izoterma Langmuira sorpcji oleju napędowego na strukturze montmorylonitu

The results indicate that Freundlich model describes the phenomenon of diesel oil sorption on clay minerals more accurately. As can be seen in Fig. 3, the experimental points fit well with the applied model, which suggests a stable, localized adsorption. Due to the heterogeneous structure of the sorbent and the construction of packages (2: 1 type) sorption may take place both on the surface of the sorbent as well as within its crystal lattice. The value of factor "1/n", which describes the diversity of free enthalpy associated with diesel oil sorption by the active centers of sorbent is crucial. In the case of montmorillonite 1/n lower than 1 indicate that with increasing concentration, diesel oil is bounded to active centers with lower free energy [4].

Results of research on the effect of clay fraction (montmorillonite) on the biodegradation kinetics are shown in Figure 5. Analyses of internal references without microorganisms have not demonstrated the phenomenon of spontaneous degradation, or volatilization of diesel oil.

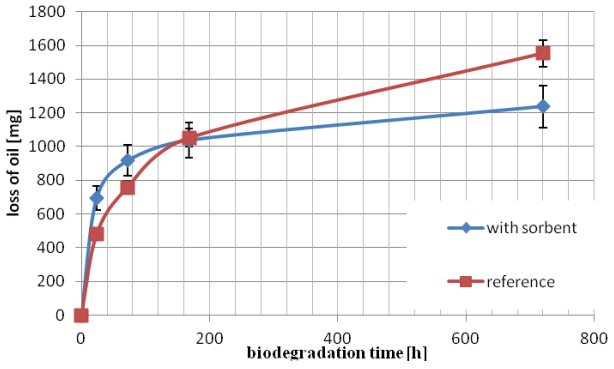

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Fig. 5. The impact of montmorillonite on diesel oil biodegradation kinetics
Rys. 5. Wpływ montmorylonitu na kinetykę biodegradacji olej napędowego

The results indicate that the addition of clay fraction results in increasing of degradation rate during the early stages of the experiment. This may be associated with reduced toxicity of system due to partial immobilization of the xenobiotic within the crystal structure of clay mineral as well

as the formation of biofilm, which may increase the microbial resistance to stress. After 10 days of the experiment, the final efficiency of biodegradation in systems containing sorbent was lower by 19% than in the case of a system without the sorbent. It is probable, that diesel oil fraction was immobilized inside of the crystal structure and simultaneously no longer bioavailable for microorganisms, which inhibited the complete hydrocarbons biodegradation.

4. Conclusions

The study indicates that mineral sorbents play an important role in the immobilization of hydrocarbon contamination. The highest sorption properties were noted for montmorillonite. Freundlich isotherm allows for modelling of sorption kinetics. It can be concluded that the diesel oil immobilization occurs not only on the surface of the mineral particles but also inside the structure. The soils richer in clay fraction are characterized by a lower risk of vertical migration of pollutants into groundwater. Analysis of the impact of the clay fraction on biodegradation kinetics showed that the soil with rich sorption complex may reduce stress for microorganisms and thus improve the rate of biodegradation in the early stages of remediation. On the other hand, immobilization of xenobiotics, which leads to reduction of bioavailable hydrocarbon fraction may also prevent the ultimate biodegradation. Therefore, in the case of contamination of soil areas with high sorption properties it is recommended to use non-toxic surfactants, which may increase the quantity of bioavailable xenobiotics and increase the efficiency of remediation.

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