

COMPARATIVE ANALYSIS OF THE ABSORBENCY OF SORBENTS DETERMINED BY VARIOUS METHODS FOR DIESEL OIL AND WHITE SPIRIT

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Abstract

The paper presents a comparative analysis of the absorbency results of selected sorbents. 6 sorbents were selected for testing: Ecobark, Eusorb, Lingosorb, Kompakt, Zugol and sand. The research was carried out using three methods: Westinghouse, capillary wicking and our own field method. The highest average absorbency values were recorded for the Westinghouse laboratory method. The results obtained using the capillary wicking method were approximately 35% lower, and those obtained using the field method similar to real conditions constituted approximately 30% of the absorbency determined by the Westinghouse method. The lowest result was achieved for a test conducted on own training ground, intended to simulate real conditions. The results show real discrepancies between the achieved absorbency values of sorbents and the type of method chosen.

Keywords: sorbents, absorption, absorbency

1. Introduction

The fire brigade is a uniformed formation that, in addition to saving people's health and lives, also takes action to protect the environment. The large amount of transported hazardous substances and their presence in road transport pose a serious threat to the environment. The activities of firefighters in the field of chemical and ecological rescue, among others, by using appropriate equipment, limit and eliminate the danger to the world around us (Dmochowska, 2019).

The first step taken to eliminate the threat after a hazardous substance leak is, first of all, to limit the spill and prevent its further spread. Then, if no combustion

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reaction occurs (pool fire), firefighters begin mechanical collection. The process can be carried out using basic equipment such as shovels, buckets, or with specialized pumps adapted to work with hazardous liquids. Then, a sorbent is applied to the surface that has been covered with a dangerous substance, with its task being to collect residues from previously performed activities (Gancarczyk, 2017).

A sorbent can be defined as a porous material used to retain and absorb various types of hazardous substances. The structure of the sorbent is based on a significant number of voids inside the grain, called pores. The two basic types of pores are open and closed. The first of these are characterized by connection with the top layer. Their main feature is the ability to allow substances to migrate into the internal structure of the material. There is no access to closed pores from the outside, but thanks to their characteristics, they have a positive effect on the material's buoyancy (Polanczyk, 2019). Sorbents can comprise all substances that have the ability to retain toxic liquids inside (absorption process) or on their surface (adsorption process), as well as those with both phenomena simultaneously (Dmochowska, 2019). Sorbents are used to absorb a wide range of substances, which include, for example, petroleum substances, oils, hydrocarbons, acids and bases (Polanczyk, 2021). An important property of the porous material used as a sorbent is primarily the lack of a chemical reaction in contact with the absorbed medium (Sobolewski, 2018; Li, 2016).

Sorbents, as substances commonly used by firefighters in rescue and firefighting activities, are characterized by many parameters. The basic practical criterion regarding the properties of sorbents is absorbency (Anuzyte, 2018). It is defined as the ratio of the mass of absorbed substance to the mass of sorbent (Polanczyk, 2018). The term absorbency determines the ability of the sorbent to absorb the liquid constituting the spill. A sorbent with a high absorbency value allows the absorption of liquid with a relatively low amount of the sorbent material itself, and the volume of material sent for disposal will be lower than in the case of using a sorbent with lower absorbency.

2. Rescue operations using sorbents

The scope of activities of the State Fire Service covers many issues related to rescue. Article 16 of the Regulation of the Minister of Internal Affairs and Administration of September 17, 2021 on the detailed organization of the national rescue and firefighting system (Polish Journal of Laws/Dz.U. of 2021, item 1737) specifies the area of activities related to chemical and ecological rescue operations. Paragraph 2, point 9 defines "binding or neutralization of hazardous substances". In many cases, these actions can be accomplished with the use of sorbents (Majder-Łopatka, 2013).

Equipment standards for firefighting vehicles provide information on the necessary fittings for rescue and firefighting vehicles. Vehicles that are available first must have at least 20 kg of sorbent in their equipment. The given value may be

increased if the specificity of the area in which the given vehicle operates requires such use (Półka, 2015).

Every year, the National Headquarters of the State Fire Service develops current statistics related to the activities of firefighters. The data below shows the number of incidents in which firefighters used sorbents (activities related to neutralization, sorption of chemical and other substances) and the amount of sorbents used (sorbent mass in kg).

In the years 2011-2021, the number of interventions ranged from 29 147 in 2013 to 46 318 in 2019. Until 2015, the number of incidents did not exceed 40 000. Since 2016, the number of cases in the country due to neutralization, sorption of chemical and other substances has become stabilized, exceeding 41 000 in each subsequent year. Between the least outbound year of 2013 and the record outbound year of 2019, the difference in events was slightly over 37%.

Another statistical aspect worth noting is the consumption of sorbents during rescue and firefighting activities, presented in Table 2. In the years 2011-2021, the number of sorbent kilograms used to eliminate chemical and ecological threats ranged from 592 277 kg in 2013 to 911 599 kg in 2016. Since 2018, the amount of used sorbents has become stabilized, exceeding the limit of 800 000 kg, but was not more than 900 000 kilograms. Until 2015, the number of used sorbents did not exceed 800 000 kilograms per year.

Comparing the first and second tables, it was found that the consumption of sorbents is closely related to the number of incidents during which neutralization, sorption of chemical and other substances were carried out. A smaller number of interventions in 2013 resulted in a lower amount of used material. The most intense year, i.e. 2019, did not bring the highest amount of substance consumed. In 2016, despite fewer trips involving neutralization, sorption of chemical and other substances, the most sorbent was used, amounting to 911 599 kilograms.

Table 1. Use of sorbents during rescue and firefighting operations in Poland in 2011-2021

Year	Number of incidents	Mass of used sorbent [kg]	Average sorbent consumption per incident [kg per accident]
2011	34071	729711	21.42
2012	30472	719038	23.60
2013	29147	592277	20.32
2014	35426	719070	20.30
2015	38564	793142	20.57
2016	43846	911599	20.79
2017	42863	796692	18.59
2018	44621	828266	18.56
2019	46318	880411	19.01
2020	44702	834117	18.66
2021	41885	822874	19.65

3. Research methodology

An experimental study of the absorbency of selected sorbents was carried out to compare the absorbency parameters of six sorbents available on the market dedicated to removing liquid spills, including the common material such as sand. The experiment was carried out in three series for each sorption material. Tests using laboratory methods were carried out for all sorbents, and the field method was carried out for the Compact sorbent.

In all methods, the absorbency of the sorbent is calculated from formula (1):

$$C = \frac{\text{mass of used sorbent} - \text{initial mass of used sorbent}}{\text{initial mass of used sorbent}} \left[\frac{\text{g}}{\text{g}} \right] \quad (1)$$

The average absorbency value was calculated using formula (2):

$$C_{\text{sr}} = \frac{C_1 + C_2 + C_3}{3} \left[\frac{\text{g}}{\text{g}} \right] \quad (2)$$

where the subscript corresponds to the method:

WEST – Westinghouse method

CAP – Capillary seeping method

FIL – Field method

Westinghouse method

The Westinghouse method involves weighing and placing the sorbent in a mesh container made in the form of a cone. The sample prepared in this way is placed on a stand and immersed in a beaker filled with liquid. After immersing the sorbent for 10 minutes, the stand was lifted and the sorbent is drained of excess medium over the beaker for 10 minutes. After draining off the excess, the sample containing the sorbent saturated with liquid should be weighed (Węsierski, 2020).

Referring to real conditions, the Westinghouse method assumes that the sorbate is accumulated and creates a pool with a low surface area but a relatively high pool depth. This creates conditions that are probably unrealistic because high-depth spills are first removed using e.g. pumps that can effectively recover part of the spilled liquid, and then, after lowering the liquid layer, a sorbent is used, thus limiting the amount of waste. This creates working conditions in which the pool has a low depth value, causing the grains of porous material not to float in the liquid but to be surrounded by it, which may constitute conditions completely different from those proposed in this method.

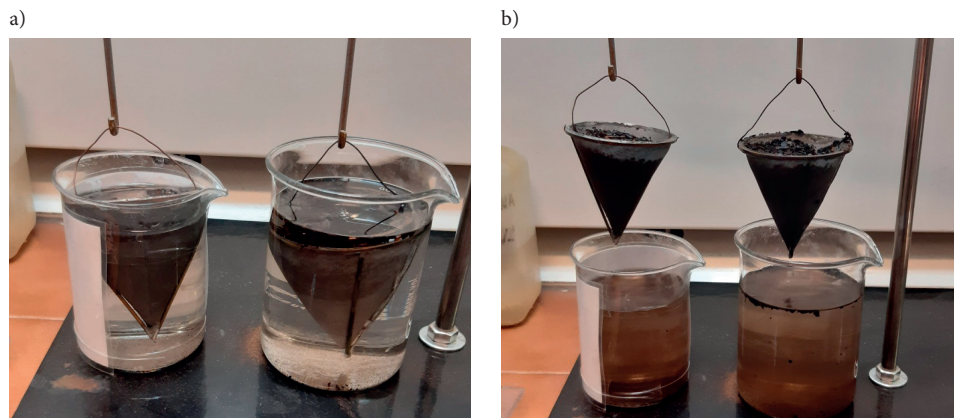


Figure 1. View of sorbent samples while immersed in sorbate (a) and while draining (b)

Capillary seeping method

In the capillary seeping method, the tested sorbent is placed in perforated syringes located on the arm of a laboratory scale that constantly monitors its weight along with the sorbent and the absorbed sorbate. The sample prepared in this way is attached to the balance arm and the end of the syringe is immersed in the dish with sorbate.

In this method, most of the sorbent placed in the syringe has no real contact with the medium because the sorbent itself is formed as a column, and the sorbate has contact only through the perforated bottom part of the syringe. Sorption is based on the phenomenon of capillary action.



Figure 2. Test stand for the capillary seeping method: 1 – laboratory scale, 2 – anti-vibration table, 3 – measuring container with sorbent, 4 – weighing dish with sorbate

Field method

The proposed own field method aims to determine the absorbency of sorbents in conditions as close as possible to real ones. The method involves marking a square of $1\text{ m} \times 1\text{ m}$ on the tested surface and pouring a hazardous liquid (sorbate) with a volume of 0.5 dm^3 . The resulting spill is loosely covered with the tested sorbent followed by a 10 minute waiting time. Then the sorbent is spread evenly over the entire test surface and left for further 10 minutes. Afterwards the collected saturated sorbent is weighed. In the first attempt, a typical amount of sorbent is used to cover the spill. In the second attempt, the amount of sorbent is reduced to maximize the amount of sorbate absorbed per unit mass of sorbent. In the last test, the smallest amount of sorbent should be used, but additional sorbent may be added in the initial part of the test.

The presented method simulates conditions similar to real ones during rescue and firefighting operations. When a firefighter arrives at the scene of an incident and begins to eliminate the spill, he spreads the sorbent at his own discretion. Covering spills with sorbent, spreading with a brush and then collecting waste are activities performed without the use of measuring equipment and only on the basis of the firefighter's experience gained from similar incidents.

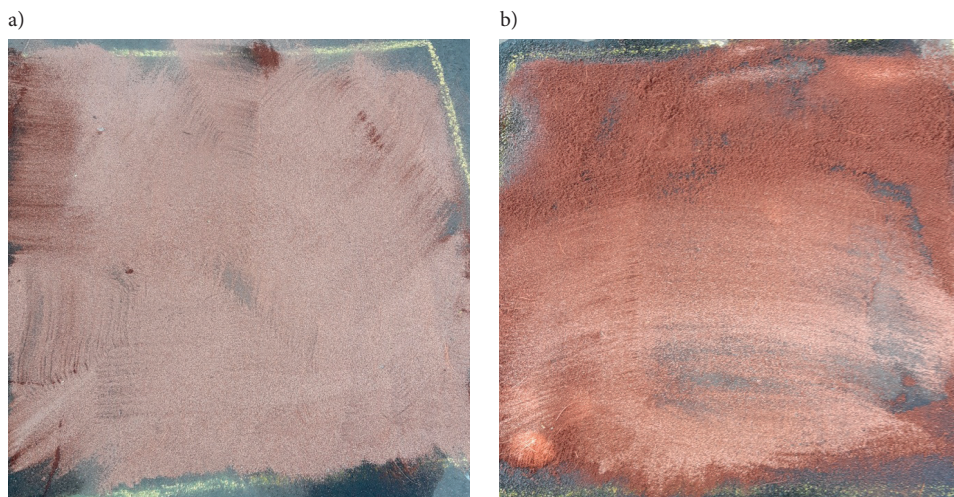


Figure 3. View of the sample with an excess of sorbent (a) and with a minimum amount of sorbent (b)

4. Research material

The following sorbents were used for the study:

1. ECOBARK – the sorbent is produced with the use of dried pine bark with the addition of previously processed pine wood fibre. Ecobark can be used to remove oils, petroleum hydrocarbons, paints, emulsions, blood, some acids and bases, both from aqueous and solid surfaces. The product has hydrophobic properties - it does not absorb water. In case of contact with strong solutions of nitric, sulfuric or hydrochloric acid, there is a risk of generating harmful gases and fire. Avoid contact with high temperatures and open flames.
 2. EuSORB – hydrophobic organic peat sorbent produced from high-quality peat that decomposes biologically. Due to its organic origin, it can be disposed of by incineration. EuSORB is intended for oil and petroleum-based liquids that can be absorbed both on hardened surfaces and from the water surface.
 3. Compact – a mineral sorbent consisting of calcined and granulated diatomaceous earth, intended for the absorption of liquid spills, both of hydrocarbon origin, acids, alkalis, solvents and solutions of chemical substances. The product is passive towards all liquids except hydrofluoric acid.
 4. Lignosorb – based on the hydrophobized hydrolysis lignin, loose sorbent intended for the removal of toxic substances.
 5. Zugol – a product made from natural bark, without the addition of chemicals. This sorbent is characterized by high absorption properties for oils, gasoline, kerosene, cutting fluids, coolants, emulsions, rinsing fluids and paints. It is prohibited to bring this sorbent into contact with nitric acid solutions. Zugol cannot be used to sorb nitric acid because it may release nitrogen fumes. Zugol is characterized by its immediate action, without the risk of slipping, or friction effects on machine parts, and is equally useful on land and on water.
 6. Sand – used for the study to compare the absorbency parameters of sorbents available on the market, produced for the purpose of absorbing spills of substances, with a commonly available material of a relatively low price.
- The tests were carried out for two hazardous liquids: diesel oil and white spirit.

5. Results and analysis

The tables below present the absorbency results of the sorbents obtained in each 3 series and the average value. The tables contain data for two types of sorbate: diesel oil and white spirit. All 6 sorbents were tested using laboratory methods, and only Compact sorbent was tested using the field method.

Table 2. Summary of absorbency results of tested sorbents using the Westinghouse method

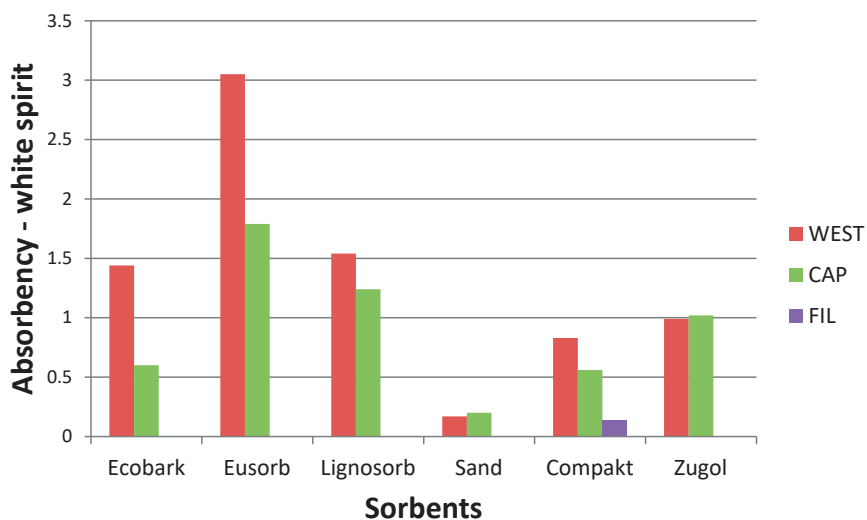
	Absorbency of sorbent					
	Ecobark	Eusorb	Lignosorb	Sand	Compakt	Zugol
White spirit						
1 st sample	1.38	4.01	1.82	0.15	0.79	1.23
2 nd sample	1.44	3.37	1.56	0.17	0.80	0.93
3 rd sample	1.49	1.76	1.24	0.18	0.91	0.82
average	1.44	3.05	1.54	0.17	0.83	0.99
Diesel oil						
1 st sample	1.08	1.70	1.87	0.21	0.89	0.92
2 nd sample	1.03	1.78	1.98	0.20	0.93	1.04
3 rd sample	1.02	1.82	2.13	0.21	0.91	1.15
average	1.04	1.76	1.99	0.21	0.91	1.04

Table 3. Summary of the absorbency results of the tested sorbents using the capillary seeping method

	Absorbency of sorbent					
	Ecobark	Eusorb	Lignosorb	Sand	Compakt	Zugol
White spirit						
1 st sample	0.47	1.83	1.22	0.20	0.56	1.12
2 nd sample	0.70	1.64	1.27	0.21	0.56	1.00
3 rd sample	0.64	1.89	1.23	0.19	0.57	0.94
average	0.60	1.79	1.24	0.20	0.56	1.02
Diesel oil						
1 st sample	0.66	2.60	1.21	0.16	0.58	0.57
2 nd sample	0.77	2.43	1.28	0.20	0.57	0.68
3 rd sample	0.54	1.13	1.16	0.17	0.59	0.73
average	0.66	2.05	1.22	0.18	0.58	0.66

Table 4. Summary of the absorbency results of the tested sorbents using our own field method

Absorbency of sorbent	
Kompakt	
White spirit	
1 st sample	0.10
2 nd sample	0.15
3 rd sample	0.17
average	0.14
Diesel oil	
1 st sample	0.14
2 nd sample	0.17
3 rd sample	0.55
average	0.29

**Figure 4.** Summary of the results of the average absorbency of sorbents tested using selected methods for white spirit

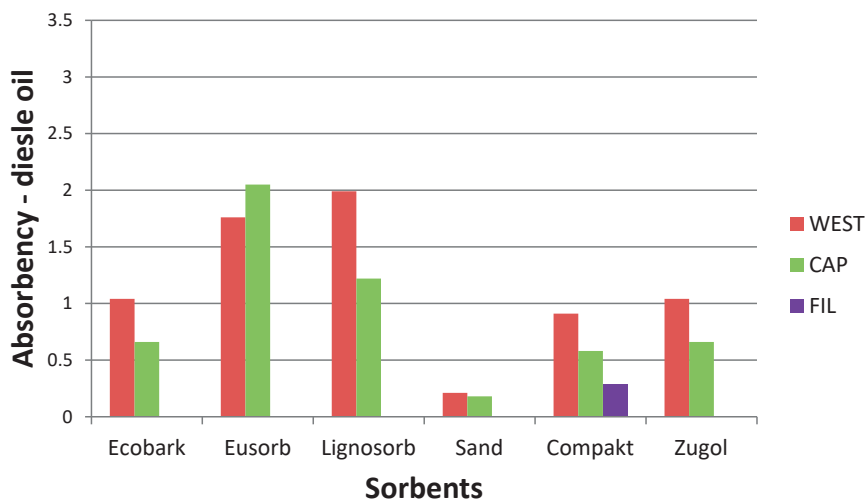


Figure 5. Summary of the results of average absorbency of sorbents tested using selected methods for diesel oil

The aim of the study was to compare the absorbency parameter for selected sorbents using two popular sorbates: white spirit and diesel oil. This study allowed establishing the absorbency parameters for selected sorbents both in laboratory conditions and in conditions similar to real ones. The results of the conducted research show the disproportion that exists between the results achieved depending on the study conducted.

First, a laboratory test using the Westinghouse method was performed. The highest results achieved in this test include the sorbents Eusorb and Lingnosorb, whose absorbency reached 3.05 and 1.54 for white spirit and 1.76 and 1.99 for diesel oil, respectively. The average values of the absorbency parameter for the remaining ones were: Ecobark – 1.44, Kompakt – 0.83, Sand – 0.17, Zugol – 0.99 for white spirit and Ecobark – 1.04, Kompakt – 0.91, Sand – 0.21, Zugol – 1.04 for diesel oil. Samples with sand had the lowest absorbency parameters.

The next test carried out was the capillary seeping method, for which the highest results of the absorbency parameter were again recorded for the Eusorb and Lingnosorb sorbents, the absorbency of which reached 1.79 and 1.24 for white spirit and 2.05 and 1.22 for diesel oil, respectively. The average values of the absorbency parameter for the remaining ones were: Ecobark – 0.60, Kompakt – 0.56, Sand – 0.20, Zugol – 1.02 for white spirit and Ecobark – 0.66, Kompakt – 0.58, Sand – 0.18, Zugol – 0.66 for diesel oil. Samples with sand have again shown the lowest absorbency parameters.

By compiling the absorbency results obtained in the capillary seeping and Westinghouse methods it becomes noticeable that when comparing the average absorbency values only in the case of the Euroisorb sorbent for diesel oil, the average value of the absorbency parameter obtained with the capillary seeping method is

higher than that obtained in the Westinghouse method. The average absorbency value for the capillary seeping method was 2.05 and for the Westinghouse method it came up to 1.76. This means that the absorbency value obtained using the Westinghouse method is approximately 13% lower than that obtained using the capillary wicking method.

As regards other sorbents, the absorption results obtained using the Westinghouse method were found to be higher than those obtained using the capillary wicking method by approximately 50% on average.

The results of tests of the Kompakt sorbent carried out on the training ground, simulating real conditions, were compared with the conditions obtained in the laboratory. The highest average absorbency value was recorded for the laboratory Westinghouse method, which amounted to 0.83 for white spirit and 0.91 for diesel oil. An approximately 65% lower result was obtained for the capillary seeping method, the value of which was 0.56 and 0.59, respectively. The lowest result was obtained for a test conducted on a training ground, which was intended to simulate real conditions. The average absorbency value for this sample was 0.14 for white spirit and 0.29 for diesel oil, which is a result approximately several-fold lower as compared to laboratory methods. The disproportion of the results obtained is caused by a different approach to determining absorbency. Laboratory methods are aimed at showing the maximum absorbency value by using the sorbate in a glass beaker and having good access to the pores in the sorbent. In fact, the liquid spreads over the surface, filling the depressions in the irregularities and creating a thin layer. In such conditions, it is difficult to collect exactly the entire amount of the spilled substance and even more difficult to use all the pores in the sorbent when it cannot be immersed in the sorbed liquid. The absorbency values obtained for the method simulating real conditions show that the amount of sorbent used depends on the ability to use the sorbent and its skilful spreading over the surface of the pool and mixing it so that the grains of the sorbent located on top can be as close as possible to the ground and the absorbed liquid. Proper use of the sorbent will significantly reduce consumption and the costs of eliminating the threat. Regardless of the selected sorbent, the absorption parameters obtained in an open system, such as a method simulating real conditions, will be lower than those obtained in closed conditions, such as those performed in the laboratory.

Summary

Sorbents are an important element of activities of the State Fire Service in the field of chemical and ecological rescue operations. Sorbents are used in most traffic incidents and other incidents involving the leakage of hazardous substances onto the ground or water. The proof of their widespread use in the activities of rescue and firefighting units is the fact that they are a basic element of a fire truck.

The purpose of the study was to compare the absorbency of six selected sorbents for white spirit and diesel oil as sorbate. This was intended to show the effectiveness of materials produced for the elimination of spills of substances, the structure of which allows the absorption of a hazardous medium inside its structure, with a common material whose structure only allows for adsorption on its surface – sand. The study utilised a well-established method for testing the absorbency of sorbents – the Westinghouse method and the capillary seeping method. Additionally, tests were carried out using our own field method, simulating real conditions for the most popular sorbent in Poland – Compact.

The best absorbent properties were demonstrated by Eusorb and Lignosorb sorbents. Both sorbents are organic sorbents based on peat and lignin fibres, respectively. Given their chemical composition, they cannot be used on spills of acids and alkalis due to the potential possibility of a chemical reaction with the sorbent. The average absorbency value of the mentioned sorbents for laboratory methods is approximately 1.5. Sand has the worst sorption properties, for which the average absorbency value is approximately 0.20 and is 4 times lower than the average absorbency of the other tested sorbents.

The results obtained in the above-mentioned tests and the comparison of the obtained sorption values point to an almost three-fold difference between the field method simulating real conditions and the laboratory methods. With respect to the results of average sorption values obtained in laboratory tests and tests simulating real conditions, rescue and firefighting units assigned with conducting chemical and ecological rescue operations should expect that the absorbency values obtained by the applied sorbent in real conditions would be significantly lower than the results obtained in the laboratory.

The key to the optimal use of sorbents in real conditions is their skilful distribution and mechanical mixing, e.g. using a brush, which is common equipment in fire trucks. This treatment allows the sorbent grains located on the surface to be moved closer to the ground and enables physical contact with the absorbed liquid, which allows the effective use of pores inside the sorbent structure. The ability to optimally use sorbents allows both to reduce the volume of generated waste and to reduce the costs incurred by the State Fire Service related to the purchase of the sorbent.

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ANALIZA PORÓWNAWCZA CHŁONNOŚCI SORBENTÓW OKREŚLANEJ RÓŻNYMI METODAMI DLA OLEJU NAPĘDOWEGO I BENZYNY LAKOWEJ

Abstrakt

W pracy przedstawiono analizę porównawczą wyników chłonności wybranych sorbentów. Do badań wytypowano 6 sorbentów: Ecobark, Eusorb, Lingosorb, Kompakt, Zugol i piasek. Badania przeprowadzono 3 metodami: Westinghouse'a, podsiąkania kapilarnego oraz własną metodą polową. Największe wartości średniej chłonności odnotowano dla metody laboratoryjnej Westinghouse'a. Wyniki otrzymane metodą podsiąkania kapilarnego były niższe o około 35%, zaś otrzymane metodą polową zbliżoną do warunków rzeczywistych stanowiły około 30% chłonności określonej metodą Westinghouse'a. Najniższy wynik osiągnięto dla badania przeprowadzonego na poligonie, mającego symulować warunki rzeczywiste. Wyniki ukazują realne rozbieżności pomiędzy osiągniętymi wartościami chłonności sorbentów od rodzaju obranej metody.

Słowa kluczowe: sorbenty, absorpcja, chłonność