



## **Environmental Aspects of Sorption Process**

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### **1. Introduction**

The perpetual progress of civilization associated with constant industry development especially in the field of transportation, chemical industry or refinery (Al-Majed et al. 2012, Piecuch and Piecuch 2013). brings the threat of uncontrolled release of hazardous substances into the environment (de Cassia et al. 2014, Polanczyk et al. 2013). Leakages of petroleum or other dangerous substances adversely affect the atmosphere, water or soil environment (Wu et al. 2014).

The substances classified as dangerous such as gasoline or petroleum, are exploited daily by most population. Therefore, the risk of environment contamination is extremely high. In case of emergency situation, e.g. a car accident where spillage of exploitation liquids appears, the Fire Department has to take actions to prevent chemical and ecological pollution (Lee and Jung 2013, Papadonikolaki et al. 2014, Zuo-fu and Jia-lin 2016). Therefore, substances with sorption properties, so-called sorbents, available in many forms, are able to collect not only petroleum substances but also other dangerous liquids, such as acids and alkalis (Demirel Bayik and Altin 2017, Dong et al. 2016, Thinakaran et al. 2008). The proper sorbent choice should include the location of the accident and the type and quantity of spilled petroleum substance (Półka et al. 2015). The ideal sorbent for cleaning oil spills should have the following features: good mutual solubility, high surface area (and/or high surface to thickness ratio), porous structure, high swelling, low degree of cross linking

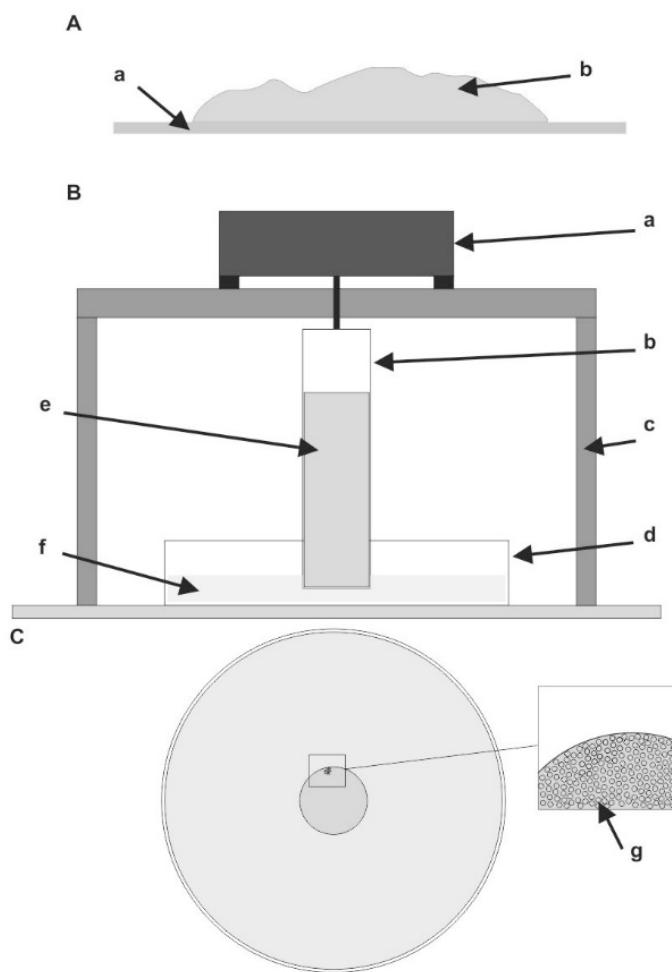
(Wu et al. 2012). In potentially hazardous situation such as car accidents, the preventive activities are dedicated to stop spreading of the dangerous substances and to bring the road surface to its pre-event state (Ting Dong et al. 2015). In such situations the choice of sorbent type is directed into sand as it is “on hand” virtually everywhere and it prevents further soil contamination. However, in the case of large-scale leakages selection of the proper type of sorbent is necessary as application of the material with the best sorption properties may limit the costs of cleaning operation (Eakalak et al. 2004). Therefore, the aim of the study was to simulate and compare sorption process of petroleum products with the use of two types of sorbents.

## 2. Materials and methods

In this study the impact of sorption process of two sorbents (dry sand and compact) in contact with different petroleum substances (diesel and gasoline) was analyzed.

A dedicated set-up was applied for the analysis of sorption process in a laboratory scale. In the real conditions, excessive amount of sorbent is used to cover spilled sorbate (Fig. 1A). However, in the laboratory scale we used weighed sorbent that was packed in a dedicated syringe and immersed in a Petri dish filled with certain volume of sorbate (Fig. 1B).

To replicate the leakage of operating fluids from a car engine chamber to the ground, a Petri dish filled with certain volume of analyzed sorbate was used. Each time a longitudinal, transparent, cylindrical container made of polypropylene (Fig. 1Bb) was filled with 50 cm<sup>3</sup> of analyzed sorbent (Fig. 1Be). A porous wall was located in the bottom of the longitudinal container to supports the contact between the sorbent and sorbate (Fig. 1Cg). The longitudinal container was hanged on the telescope joined with the electronic weight (Fig. 1Ba) placed on the anti-vibration table (Fig. 1Bc).. Each time the longitudinal container was immersed in 100cm<sup>3</sup> volume of sorbate (Fig. 1Bf), placed in the Petri dish (Fig. 1Bd). The weight gain of the sorbate which penetrated the sorbent placed in a longitudinal container (Fig. 1Bb) was measured constantly with an electronic scale (mean error of the scale was equal to 2 mg). Data were recorded every 10 s, until the same value repeated three times at the scale monitor.



**Fig. 1.** A scheme of analyzed sorption process and experimental set-up, composed of: Part A real conditions – a) sorbate, b) sorbent; Part B (side view): a) an electronic weight, b) a cylindrical container for analyzed sorbent, c) an anti-vibration table, d) a Petri dish e) sorbent, f) sorbate; Part C (top view): g) porous bottom of a cylindrical container for analyzed sorbent

**Rys. 1.** Schemat procesu sorpcji i eksperymentalnego układu, składający się z: Część A rzeczywiste warunki – a) sorbent, b) sorbat; Część B (widok z boku): a) elektroniczna waga, b) cylindryczny pojemnik na analizowany sorbent, c) stół antywibracyjny, d) płytka Petriego, e) sorbent, f) sorbat; Część C (widok z góry): g) porowate dno cylindrycznego pojemnika na analizowany sorbent

Two operating fluids, diesel and gasoline (Table 1), in the final volume of 100cm<sup>3</sup> were analyzed in different proportions (100% of gasoline or 100% of diesel; 50% of gasoline and 50% of diesel; 25% of gasoline and 75% of diesel; 75% of gasoline and 25% of diesel) and were exposed to two different types of sorbents, dry sand and compact (Table 1). Each time the sorption process was performed until no change in sorbate mass, recorded by scale, was detected. Also, reference sorption processes for 100% of gasoline and diesel were included. This approach allowed to compare the influence of volume proportion of both sorbates on the sorption process.

The analyses were performed for the following conditions: room temperature (20°C) and air relative humidity approximately 60%. The set-up was placed under a laboratory hood to avoid the influence of uncontrolled wind flow.

**Table 1.** Properties of analyzed sorbents and sorbates

**Tabela 1.** Właściwości analizowanych sorbentów i sorbatów

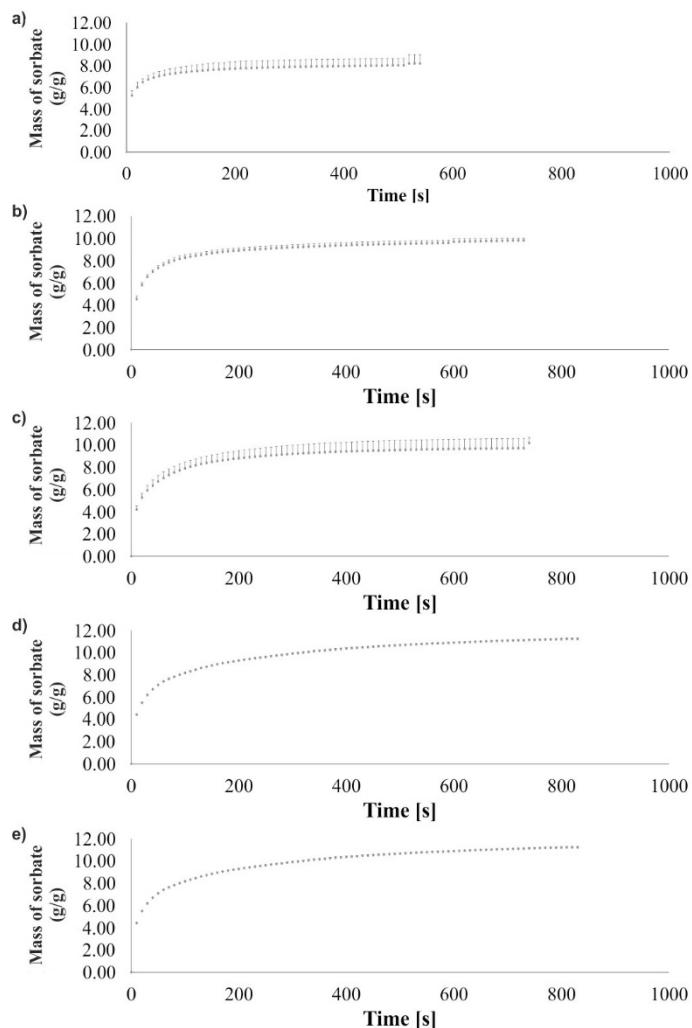
Properties	Dry sand	Compact	Diesel	Gasoline
Density (g/cm <sup>3</sup> )	2.62	0.52	0.70	0.82
Size of grain (mm)	0.05-2.0	0.30	—	—
Viscosity (Pas)	—	—	0.83	0.80
Surface tension (mN/m)	—	—	28.40	24.65
Specific surface area (m <sup>2</sup> /g)	—	—	0.1	18.00

Measurements were done in triplicates and presented as mean±standard deviation (SD).

### 3. Results

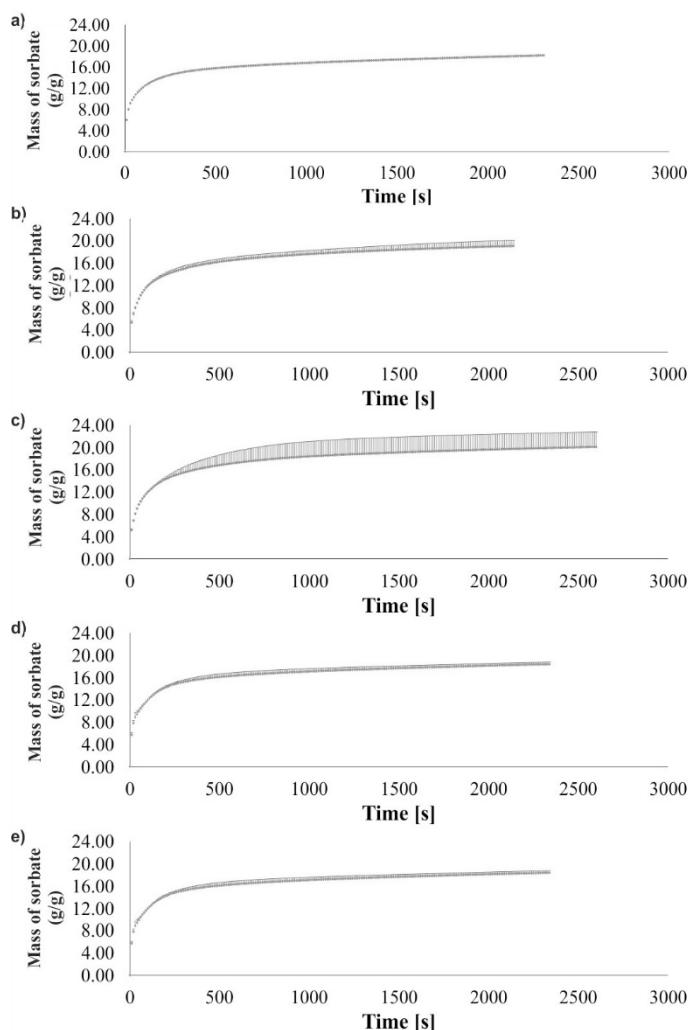
In this study we investigated the influence of applied sorbent and sorbate on the intensity of sorption process. At first 100% of each sorbate (gasoline and diesel) was investigated for both sorbents: compact and dry sand (Fig. 2a-b and Fig. 3a-b). Sorption for dry sand was equal to  $0.12 \pm 0.010$  g/g and  $0.14 \pm 0.004$  g/g for gasoline and diesel, respectively. While, for compact sorbent sorption was equal to  $0.64 \pm 0.003$  g/g and  $0.66 \pm 0.038$  g/g for gasoline and diesel, respectively. Similar trend, however with an increase in sorption intensity, was observed for both sorbents which contacted with the mixture of sorbates where: 50% was gasoline and 50% was diesel (Fig. 2c and Fig. 3c). Here the sorption process was equal to  $0.14 \pm 0.013$  g/g and  $0.71 \pm 0.093$  g/g for dry sand and compact sorbent, respectively. Moreover, further increase of the gasoline percentage in analyzed sorbate mixture (75% of gasoline and 25% of diesel) decreased sorption for dry sand to  $0.12 \pm 0.011$  g/g. This value was equal to sorption of pure gasoline. Similar analysis made for compact indicated that sorption was equal to  $0.65 \pm 0.018$  g/g, which was between the values received for pure gasoline and pure diesel. Finally, with the decrease of gasoline percentage in the analyzed sorbate mixture (25% of gasoline and 75% of diesel) sorption for dry sand was equal to  $0.14 \pm 0.012$  g/g, which was comparable to 100% of diesel (Fig. 2e and Fig. 3e).

Moreover, the time of sorption was analyzed. The sorption time for concentrated diesel was  $697 \pm 94.5$  s and  $2180 \pm 52.9$  s for dry sand and compact, respectively. Interestingly, the sorption time of pure gasoline was  $533 \pm 20.8$  s and  $2325 \pm 21.2$  s for dry sand and compact, respectively. Therefore, sorption time for pure gasoline was longer compared to the diesel for both tested sorbents. Additionally, an increase in sorption process time was observed for increased concentration of diesel in sorbate mixture. For a mixture of 25% of gasoline and 75% of diesel sorption was equal to  $845 \pm 21.2$  s and  $2660 \pm 102$  s for dry sand and compact, respectively. When concentration of diesel was lower compared to gasoline (75% of gasoline and 25% of diesel) additional changes of sorption time were observed ( $860 \pm 42.4$  s and  $2510 \pm 240.4$  s for dry sand and compact, respectively). Furthermore, an increase of sorption time was noticed for 50% of gasoline and 50% of diesel compared to concentrated sorbate ( $740 \pm 10.0$  s and  $2675 \pm 106.1$  s for dry sand and compact, respectively).



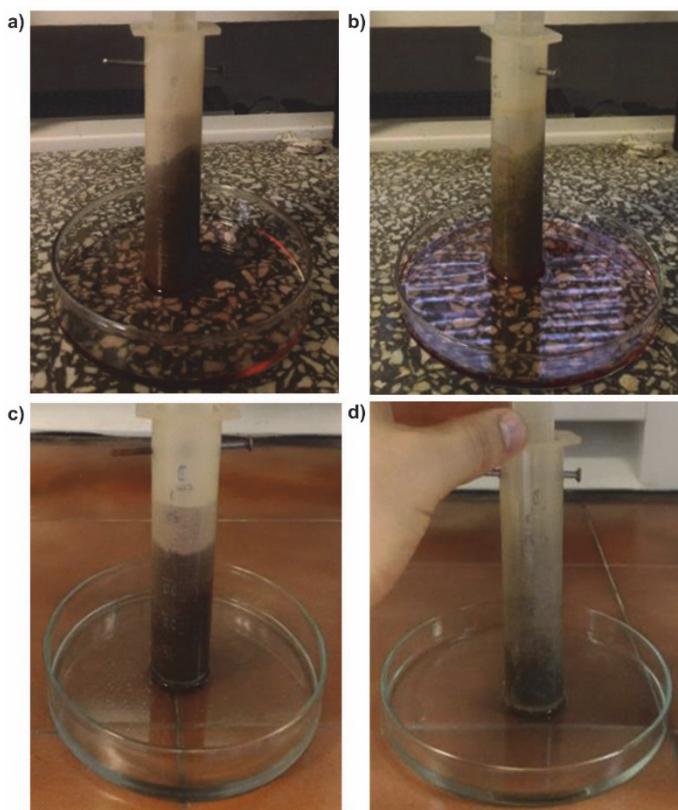
**Fig. 2.** Sorption process for dry sand in function of time for: a) 100% gasoline; b) 100% diesel; c) 50% gasoline 50% diesel; d) 75% gasoline 25% diesel; e) 25% gasoline 75% diesel. Results are presented as mean $\pm$ SD

**Rys. 2.** Proces sorpcji dla suchego piasku w funkcji czasu dla: 100% benzyny; b) 100% diesla; c) 50% benzyny i 50% diesla; d) 75% benzyny i 25% diesla; e) 25% benzyny i 75% diesla. Wyniki sa przedstawione jako średnia $\pm$ odchylenie standardowe (SD)



**Fig. 3.** Sorption process for compact sorbent in function of time for: a) 100% gasoline; b) 100% diesel; c) 50% gasoline 50% diesel; d) 75% gasoline 25% diesel; e) 25% gasoline 75% diesel. Results are presented as mean $\pm$ SD

**Rys. 3.** Proces sorpcji dla sorbentu compact w funkcji czasu dla: 100% benzyny; b) 100% diesla; c) 50% benzyny i 50% diesel; d) 75% benzyny i 25% diesel; e) 25% benzyny i 75% diesel. Wyniki sa przedstawione jako średnia $\pm$ odchylenie standardowe (SD)



**Fig. 4.** An example of sorbate profiles for: a) compact for 50% of gasoline and 50% of diesel; b) dry sand for 50% of gasoline and 50% of diesel; c) compact for 100% of gasoline; d) dry sand for 100% of gasoline

**Rys. 4.** Przykład profilu sorbatu dla: a) sorbent compact dla 50% benzyny i 50% diesel; b) suchy piasek dla 50% benzyny i 50% diesel; c) sorbent compact dla 100% benzyny; d) suchy piasek dla 100% benzyny

Finally, a profile of sorbate in a dedicated container filled with dry sand or compact was analyzed. Each time the profile of sorbate (gasoline as well as diesel) for compact had a regular shape (Fig. 4b and Fig. 4d), while for the dry sand sorbate profile was irregular (Fig. 4a and Fig. 4c).

## 4. Discussion

This paper presents the results of sorption process of two petroleum products, gasoline and diesel, with the use of two types of sorbents, dry sand and compact. Gathered data showed that the effectiveness of sorption process is higher, and the sorption process is longer for compact sorbent compared to dry sand. These results were in line with Patrushev et al. who analyzed the properties of capillary columns with synthetic sorbents (Patrushev et al. 2015). Also, Choi et al. investigated biodegradable waste as sorbent material for oil spill cleanup (Idris et al. 2014), and Bandura et al. applied similar procedure to determine sorption of clinoptilolite towards diesel and biodiesel oils (Bandura et al. 2015).

In our paper sorption for dry sand was equal to 0.12 g/g and 0.14 g/g for gasoline and diesel, respectively. Similarly other authors examined sand in contact with diesel, however in glass column and smaller amount (Michel 2005). Michel noticed that sorption for sand and diesel was in range of 0.03-0.05 g/g (Michel 2005). While, Zadaka et al. received sorption equal to 0.17 g/g after connection of sand and diesel (Zadaka-Amir et al. 2013). Those results were close to Carmody et al. who received sorption in range 0.2-0.3 g/g(Carmody et al. 2007). Therefore, our results are in line with data received by other authors.

This study has the following limitations: the area of sorbent activity was restricted to cylindrical container's wall, while in real conditions sorbent is freely spilled. Moreover, we did not include stirring of sorbent and sorbate which could increase the intensity of sorption process.

## 5. Conclusions

To sum up, comparison of compact sorbent and dry sand indicated that the effectiveness of sorption process is 6-times higher for compact sorbent compared to dry sand. Additionally, the time of sorption process was 4-times longer for compact sorbent in comparison to dry sand which correlated with higher volume of absorbed liquid. Therefore, the results indicated that a compact sorbent in contact with petroleum substances i.e. gasoline or diesel is a better solution compared to dry sand. Moreover, compact sorbent is non-flammable substance, hence it does not pose an additional threat, even if rescuers do not have full knowledge about the collected medium. However, the dry sand is a suit-

able material for limiting of the area covered with potentially dangerous liquids especially in places where commercial sorbents are unavailable, and the area is covered with potentially dangerous liquids.

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## Środowiskowe aspekty procesu sorpcji

### Streszczenie

Substancje sklasyfikowane jako niebezpieczne, tj. benzyna czy ropa naftowa, są codziennie wykorzystywane przez ludzi. Ich stosowanie związane jest bezpośrednio z wysokim ryzykiem zanieczyszczenia środowiska np. w wyniku wypadku samochodowego. W przypadku wycieku stosuje się substancje umożliwiające zabezpieczenie miejsca zdarzenia, tj. sorbenty. Z tego też względu celem badania była analiza w jakim stopniu proces sorpcji zależy od rodzaju zastosowanego sorbentu, sorbatu, a także ich proporcji. Eksperymenty prowadzono w skali laboratoryjnej, w której dwa płyny eksplotacyjne, tj. olej napędowy i benzyna, były mieszane na płytce Petriego w różnych proporcjach w łącznej objętości 100 cm<sup>3</sup>. Analizowane płyny eksplotacyjne wystawiano na działanie dwóch różnych typów sorbentów: komercyjny sorbent „compact”

i suchy piasek. Waga sorbatu penetrującego sorbent była odczytywana co 10 s przy pomocy elektronicznej wagi. W celu odwzorowania rzeczywistych warunków, w których płyny eksplotacyjne po wycieku mieszają się, sorbaty były analizowane jako mieszaniny w następujących proporcjach: 100% do 0%, 0% do 100%, 50% do 50%, 25% do 75% i 75% do 25% (odpowiednio dla oleju napędowego i benzyny). Co więcej, w celu wyznaczenia referencyjnych punktów badania wykonano również dla czystych sorbatów. Na podstawie otrzymanych wyników opracowano wykresy procesu sorpcji dla dwóch sorbentów i dwóch sorbatów w funkcji czasu. Proces sorpcji dla suchego piasku wynosił odpowiednio  $0,12 \pm 0,010$  g/g i  $0,14 \pm 0,004$  g/g dla benzyny i oleju napędowego (100% udział analizowanych sorbatów). Podczas gdy dla komercyjnego sorbentu „compact” sorpcja wynosiła odpowiednio  $0,64 \pm 0,003$  g/g i  $0,66 \pm 0,038$  g/g dla benzyny i oleju napędowego (100% udział analizowanych sorbatów). Podobny trend procesu sorpcji zaobserwowano w przypadku kontaktu komercyjnego sorbentu „compact” z mieszaniną sorbatów (50% benzyny i 50% oleju napędowego udziału analizowanych sorbatów). Wówczas proces sorpcji wynosił odpowiednio  $0,14 \pm 0,013$  g/g i  $0,71 \pm 0,093$  g/g dla suchego piasku i komercyjnego sorbentu „compact”. Co więcej, przeanalizowano, który sorbat wywiera większy wpływ na proces sorpcji. W tym celu analizowano mieszaninę sorbatów w następujących udziałach: 75% do 25% i 25% do 75% dla benzyny i oleju napędowego. Uzyskane wyniki wskazują, iż dla benzyny i oleju napędowego (25% do 75%) proces sorpcji wynosił  $0,14 \pm 0,012$  g/g dla suchego piasku. Natomiast dla komercyjnego „compactu” sorpcja wynosiła  $0,65 \pm 0,018$  g/g. Również w badaniach analizowano czas procesu sorpcji. Otrzymane wyniki wskazują, iż czas procesu sorpcji dla suchego piasku w połączeniu z olejem napędowym i benzyną był około 4 razy krótszy w porównaniu do komercyjnego sorbentu „compact”. Podsumowując należy uznać, iż komercyjny sorbent „compact” bez względu czy jest stosowany do czystych płynów eksplotacyjnych czy też do mieszanin jest wydajniejszy w porównaniu do suchego piasku.

## Abstract

Substances classified as dangerous such as gasoline and petroleum, are used daily by most of population. Therefore, they pose a potential threat of environment contamination for example in case of emergency, e.g. car accidents. This study aimed to simulate and compare sorption process of petroleum products with the use of two types of sorbents.. To replicate the leakage of operating fluids from a car engine chamber to the ground, a Petri dish filled with  $100\text{ cm}^3$  volume of analyzed sorbate was used. Fluids were exposed to two different types of sorbents such as compact and dry sand. The weight gain of the sorbate which penetrated the sorbent was measured every 10 s with an electronic scale.

Analyzed sorbents, diesel and gasoline, were tested in the following proportions: 100% to 0%, 0% to 100%, 50% to 50%, 25% to 75% and 75% to 25% (diesel to gasoline, respectively). The figures of sorption processes for different types of sorbents and sorbates in function of time were prepared. Sorption process for dry sand was equal to  $0.12\pm0.010$  g/g and  $0.14\pm0.004$  g/g for concentrated gasoline and diesel, respectively. While, for compact it was  $0.64\pm0.003$  g/g and  $0.66\pm0.038$  g/g for gasoline and diesel, respectively. Similar trend, however with an increase in sorption intensity, was observed for both sorbents contacted with equal mixture of sorbates (50% of gasoline and 50% of diesel). Here, sorption process was equal to  $0.14\pm0.013$  g/g and  $0.71\pm0.093$  g/g for dry sand and compact, respectively. Moreover, further increase of the gasoline percentage in analyzed sorbate mixture (75% of gasoline and 25% of diesel) decreased sorption for dry sand to  $0.12\pm0.011$  g/g. Moreover, sorption time for pure gasoline was 4-times longer for compact sorbent in comparison to dry sand which corresponds with higher volume of absorbed liquid. Also, sorption process was 6-times higher for compact sorbent compared to dry sand. Therefore, the results indicated that a compact sorbent in contact with petroleum substances i.e. gasoline or diesel is a better solution compared to dry sand. However, the dry sand is a suitable material for limiting of the area covered with potentially dangerous liquids especially in places where commercial sorbents are unavailable, and the area is covered with potentially dangerous liquids.

**Slowa kluczowe:**

sorpca benzyny, sorpcja diesla, sorpcja paliwa, piasek sorbent compact

**Keywords:**

gasoline sorption, diesel sorption, petroleum sorption, sand sorbent compact