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Hydrophobization of diatomaceous earth used to remove oil pollutants

Introduction

Various types of sorbents, due to their affordability, great variety and high efficiency are highly valued in remediation processes. The use of sorbents for the removal of oily substances allows the transition of pollutants from the liquid phase to the semi-solid phase, which makes it possible to effectively remove them from the environment (Adebajo et al. 2003; Deschamps et al. 2003; Chen et al. 2016; Galblaub et al. 2016; Nnaji et al. 2016; Periasamy et al. 2017; Czikkely et al. 2018; Bhardwaj and Bhaskarwar 2018; Bigui et al. 2019; Li et al. 2019; Yao et al. 2019; Kafle et al. 2019; Kukkar et al. 2020; Bai et al. 2020; Abdel-Aty et al. 2020; Zamparas et al. 2020; Han et al. 2021).

The European economy is working tirelessly to reduce the consumption of petroleum-based products but despite extensive efforts by scientists and governments of EU countries, the demand for petroleum products is still very high. Online publications, cited in the

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following work, provide recent statistics on international trade in energy products and information on the EU's main partners and on Polish trends of fuel demand for a period of ten years (Kamyk and Kot-Niewiadomska 2021; Investopedia, Mahmoud et al. 2021; Eurostat 2022).

The widespread use of petroleum products contributes to the release of petroleum substances to the natural environment, causing the extensive contamination of soil, water and air. Released pollutants cause a reduction in soil plasticity, destroy ecosystems, weaken natural biodegradation, cause the extinction of some plant and animal species and create vast migrating spills. Additionally, petroleum-derived substances show mutagenic and carcinogenic effects for both animals and humans (Gray et al. 2013; Bhattacharjee and Dutta 2022; Haque et al. 2022; Bala et al. 2022; Shukla et al. 2022). Due to the abovementioned factors, the removal of petroleum pollutants is a priority action for the benefit of the natural environment.

Mineral sorbents such as zeolites, perlite, diatomite and clay rocks in particular are eagerly used to remove petroleum pollutants (Teas et al. 2001; Rouliaa et al. 2003; Bastani et al. 2006; Machado et al. 2006; Wanga and Peng 2010; Ali et al. 2012; Pijarowski and Tic 2014; Davoodi et al. 2019; Han et al. 2021). Mineral sorbents in the form of granules work well even in hard to reach places both when removing pollutants from the water surface and from the soil. Sorption sleeves are an indispensable aid for limiting the leak zone and absorbing oil as close as possible to the leak source. Synthetic zeolites have also been used for many years, but their commercial application remains expensive (Szerement et al. 2021; Tauanov et al. 2020). Therefore, the production of low cost mineral sorbents is still a valid research topic (Guo et al. 2018; Mahmoud et al. 2021; Shadi et al. 2021; Xu et al. 2022; Li et al. 2022; Venkatesan et al. 2022).

Experts in this field of research emphasize that a particular problem with sorbent usage is the fact that many of them, especially mineral sorbents, are very sensitive to moisture. The absorbability of these materials can be reduced by using the hydrophobization process (Teas et al. 2001; Deschamps et al. 2003; Rouliaa et al. 2003; Vogt and Płachta 2017; Bigui et al. 2019; Bai et al. 2020; Han et al. 2021; Hydroperl). This kind of modification of sorbents makes them more useful in the natural environment, which is usually highly humid. The topic of the hydrophobization of different materials is as relevant as the research on new mineral sorbents. Such research could potentially contribute to improvements in oil waste purification processes. Table 1 shows the current trends in the methods of the hydrophobization of mineral adsorbents on a laboratory and industrial scale. The variety of the analyzed sorbents and hydrophobization agents indicate a wide range and multidirectional nature of research which has been performed by other researchers and under personal supervision.

Requirements for sorbents used by chemical rescue units are included in the Ordinance of the Minister of Interior and Administration of April 27, 2010. According to this ordinance, materials should be characterized by, among other techniques, the Westinghouse's method (Regulation ME 2010; Sintac Polska).

Table 1. Trends in the methods of hydrophobization of mineral adsorbents (Vogt et al. 2021)

Tabela 1. Trendy metod hydrofobizacji adsorbentów mineralnych

Sorbents	Modifier	Modification method
Magnetic adsorbents based on vermiculite-iron (Machado et al. 2006)	epoxy resin	coating
	polystyrene improving	
Dolomite (Davoodi et al. 2019)	palmitic acid	dip-coating
Vermiculite (nanotubes) (Moura and Lago 2009)	carbon nanotubes (CNT)	vapor deposition (CVD)
Diatomite (IMDC) (Han et al. 2021)	ISOBAM-104	doping, thermal treatment
Perlite 180	stearic acid	vapor phase
Perlite1 180	stearic acid	coating
Vermiculite fine		
Perlite 180	Sarsil H-15 – silicone preparation	dip-coating
Vermiculite fine		
Perlite (Hydroperl)	silicone preparation	dip-coating
Diatomite (compakt) (O.S.P, Sintac.pl)	calcination	thermal treatment

Another method of testing sorbent absorbency is the procedure included in the technical sheet of the Hydroperl product by Perlipol (Hydroperl). The literature also describes methods of testing oil sorption from the soil surface (Łuksa et al. 2010).

1. Experimental

1.1. Composites

The research was performed on diatomaceous earth, DAMSORB®K (granulate with a grain size of 0.5–1 mm) produced by IM-POL (IM-POL) and on stearic acid as a modifier (STANDARD). Tested material has been approved by the Scientific and Research Centre for Fire Protection in Józefów (CNBOP-PIB) as an agent suitable for removing oil contaminants from flat surfaces.

Diatomaceous earth is a very good environmentally friendly adsorbent of natural origin. In many studies, it has been proven that diatomaceous earths are an excellent sorbent for many compounds, both inorganic and organic. Depending on the modifications used, they have the ability to absorb oil and petroleum contamination (Elsayed 2011; Guo et al. 2018; Sriram et al. 2020; Touina et al. 2021; Xu et al. 2022; Li et al. 2022).

The tested material consists mainly of opal – a substance with the tetrahedral system of $[SiO4]^{-4}$ ions. The content of silicon dioxide in the material can range from 60 to 92%. The bulk density of the material is 552.4 kg/m^3. Diatomites are hydrophilic in nature, which means that they have a greater affinity for water than for non-polar compounds. To be used in humid conditions, they must be chemically modified.

1.2. The diatomaceous earth hydrophobization

There are many known methods for the hydrophobization of solids, but it is especially difficult to hydrophobize crushed materials. The process of hydrophobization of fine-dispersional materials has been conducted and described many times in cited literature (Vogt 2011, 2013; Buczek and Vogt 2014; Vogt et al. 2019, 2021). The raw material contained 0.74% moisture. Such a low degree of moisture in the tested material allows the hydrophobization process to be conducted without prior drying of the samples. The diatomite hydrophobization method used in this work consisted of immersing the material in a stearic acid methanol solution. After a specified time, the solvent was evaporated and the material was dried at room temperature (approx. 25°C). The concentration of the stearic acid solution (7.5% w/w), the time (1 h) and other conditions of the hydrophobization, such as temperature, drying conditions were selected experimentally.

During the drying process, some of the material clumped up. The hydrophobized sorbent was gently shredded with a laboratory rod. The properties of the material were tested seven days after the production process.

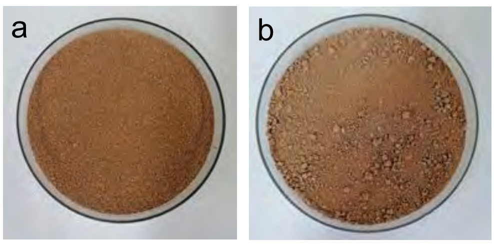

Fig. 1. Photos of the raw materials and the materials after hydrophobization

Rys. 1. Zdjęcia materiału surowego i po procesie hydrofobizacji

1.3. The hydrophilization degree of diatomaceous earth

The evaluation of the hydrophobic properties of the materials was performed based on the results obtained from the tests: water absorption (EN 1097-6:2022), Westinghouse's method (Szułczyńska et al. 2020; UNI CEN/TS 15366), floating on the water surface test and the contact angles (Washburn 1921; Buckton and Newton 1986; Alghunaim et al. 2016; Tohry et al. 2020) were determined with the use of Rame-Hart model 90 Pro Edition (PN 90-U3-PRO) apparatus.

1.3.1. Floating on water test

The floating on the water surface test consisted of placing a small amount of material on the surface of water in a beaker. The hydrophobization degree was evaluated based on the amount of material floating on the surface for a specified time. Figure 2 presents photographs of the floating on the water test for the materials obtained immediately after placing the samples on the water surface.

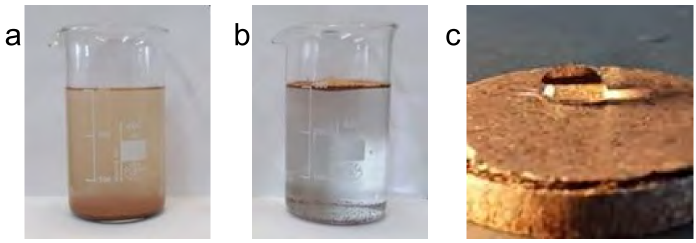

Fig. 2. Photos of tests of evaluation of the hydrophobic properties
a) and b) raw and hydrophobic material floating on the water immediately after placing the material on the surface, c) a drop of water on the compressed material

Rys. 2. Zdjęcia badań określających właściwości hydrofobowe materiału
a, b) surowy i hydrofobizowany materiał podczas próby pływania po powierzchni wody, zaraz po zrzuceniu materiału na powierzchnię, c) kropla wody na sprasowanym materiale

1.3.2. Water absorption

At first, water adsorption was determined by means of a modified method based on the EN 1097-6:2022 standard (EN 1097-6:2022). The test amount (4 g) of material was placed in a beaker and completely immersed in the water (100 cm^3). After that (1 h) the samples were filtered on a paper filter under atmospheric pressure. The sample remained in the filter for a certain time until the water stopped dripping.

The mass of the saturated portion of material was measured. The water absorption (*WA*) was calculated from Formula 1.

$$WA\ (\%) = \frac{m_1 - m_2}{m_2} \cdot 100 \tag{1}$$

m_1 – mass of the saturated material (g),
m_2 – mass of the oven-dried at 105°C material (g).

The Westinghouse's method is used by CNBOP-PiB (Scientific and Research Centre for Fire Protection) to assess the absorption capacity of petroleum pollutants by sorbents used by fire brigades (Szułczyńska et al. 2020). They can be used not only to assess the absorption capacity of petroleum pollutants but also to measure water absorption (Szułczyńska et al. 2020; UNI CEN/TS 15366). The study was performed for both raw and hydrophobized diatomite. The obtained results are presented in Table 2.

1.4. The sorption of petroleum-derived compounds

Tests of the sorption of petroleum-derived compounds were performed based on three procedures: in accordance with the technical sheet of the leading producer of hydrophobic sorption materials in Poland (Hydroperl), the Westighouse's method (Szułczyńska et al. 2020) in the oil layer and the Westighouse's method on a flat surface. A typical diesel oil with a density of 845 g/cm^3 was used for the study (SPL2403 2006).

The sorption of petroleum-derived substances according to procedure based on the technical sheet of the leading producer of hydrophobic sorption materials in Poland (Hydroperl) was made in the following way. The sample of the sorbent was placed in a glass container and distilled water was added. Then 15 cm^3 oil was added and it was extracted by shaking for 10 min. After that time, the material was separated by means of a porous plunger. The separated solution was poured into a measuring cylinder, and after the oil was separated from the water, the volume of the non-absorbed oil was measured. The absorption (*ABS*) of oil was calculated on the basis of Formula 2. The obtained values were converted into weight units. The average loose density of the samples was taken as the sample density. The results are presented in Table 2.

$$ABS = \frac{15 - V_x}{25} \cdot 1000 \left(\frac{\mathrm{dm}^3}{\mathrm{m}^3} \right) \quad (2)$$

V_x – the volume of non-absorbed diesel fuel [cm^3].

Table 2. The values of oil and water sorption

Tabela 2. Wartości sorpcji oleju i wody

Material	Oil and water sorption (% w/w) based on procedure				
	ABS (Hydroperl)	Westinghouse's method			WA (EN 1097-6:2013)
		(W1) (Szułczyńska et al. 2020)		(W2) (Szułczyńska et al. 2020)	
	oil	water	oil	water	water
Raw	12.5	112	80	107	134
Modified	35.5	27	74	92	90

The absorption of oil measured by Westinghouse's method ((W1) – from an oil layer) was calculated using Formula 1. The results are presented in Table 2.

When Westinghouse's method of oil sorption from a flat surface (W2) was used, the oil was added in small amounts to the sorbent surface until the sample was saturated. The sorbate dosing was completed when oil flow was observed on the surface of the material. Based on the mass of absorbed sorbate, the sorbent absorbency was calculated from Formula 1. The results are presented in Table 2.

1.5. Bulk density measurement

Modified sorbents should not change their weight during hydrophobization. A material that is too heavy will not stay floating on the surface of the water. The material that is too light will be removed from the application site by natural air movement. In the work, the packed and loose bulk density of the tested materials was measured.

Table. 3. Packed and loose bulk density (kg/m^3)

Tabela 3. Gęstość nasypowa luźna i upakowana (kg/m^3)

Material	Bulk density	
	packed	loose
Raw	612.2	552.4
Modified	583.8	532.7

2. Discussion

During the observation of the differences in the behavior of the sample on the water surface (Figure 2), it was objectively found that the modified material had hydrophobic properties. After seven days, the modified material was still floating on the surface of the liquid.

The average value of the contact angle for the modified sample is 104 degrees. It was not possible to determine the contact angle on a tablet made of raw material.

The modified samples are characterized by a much lower level of water absorption (*WA*) (Table 1) than the raw material. The water absorption values obtained both on the basis of the standard (*WA*) and the Westinghouse's method prove the good hydrophobic properties of diatomite after the hydrophobization process.

Oil adsorption obtained from Westinghouse's method is greater for raw material than for the modified sorbent. In the case of the oil adsorption values obtained in accordance with the procedure based on the technical sheet of the leading producer of hydrophobic sorption materials, the relationship is the opposite.

After analyzing the obtained results, it can be concluded that the modification process improves the sorption capacity of diatomite in conditions where oil pollutions are surrounded by a large amount of water. The higher value of the *ABS* parameter for the modified material indicates a significant increase in the sorption capacity of diatomite in the water environment. Under such conditions, the raw sorbent is not very absorptive and is therefore of little use. The results obtained by Westinghouse's method on the dry surface of the sorbent confirm this conclusion because in this study, the raw material is characterized by a higher oil adsorption value. However, it should be taken into account that in a polluted environment, moisture usually coexists alongside oil pollution. Thus, the sorbent used does not remain dry in contact with contaminants, as is the case in laboratory conditions. The modified diatomite will therefore show better efficiency in the environment even when used on the surface of soil.

The measurements of the loose and packed bulk density shows a slight decrease (about 4%) of the these values (Table 3) for the hydrophobized sample in relation to values of these properties for the raw sample. This relationship will be beneficial during the sorbent application.

Conclusions

The method of diatomite hydrophobization was developed and process conditions were selected experimentally.

The modified sorbent floated very well on the surface of the water – its hydrophobic properties are much better after modification. The modified sorbent has a lower water absorption capacity (*WA*) than the raw material. The average value of the contact angle for the modified sample is 104 degrees. The material is super hydrophobic.

In the water environment, the hydrophobized samples have a higher absorption capacity in relation to oil contaminations compared to the raw material. The hydrophobization process leads to an increase in the selectivity of the modified sorbent in the water environment.

The hydrophobization of the material did not significantly affect the value of the bulk density of the material – it is beneficial in the perspective of using the sorbent to remove contaminants from the water surface and the soil surface.

The use of cheap stearic acid as a modifier is economically advantageous.

Features of the modified sorbent such as good buoyancy on the water surface, low affinity to water and better absorption of oil from the solution make it possible to use the material to remove petroleum contamination from water and highly moist surfaces.

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HYDROPHOBIZATION OF DIATOMACEOUS EARTH USED TO REMOVE OIL POLLUTANTS

K e y w o r d s

hydrophobization, diatomaceous earth, oil pollutants

A b s t r a c t

Contamination of the natural environment with petroleum pollution is still a frequent and particularly dangerous phenomenon, thus there is a need to remove these pollutants. Various types of mineral sorbents (silicate minerals, zeolites, perlite, diatomite, clay rocks) are highly valued in remediation processes due to their affordable, big selectivity and high efficiency. However, many sorbents are not resistant to moisture, which limits their use. The hydrophobization process improves the effectiveness of sorbents used in a humid environment. The DAMSORB produced by IM-POL was hydrophobized with a methanolic stearic acid solution. The use of cheap stearic acid as a modifier is economically advantageous. The evaluation of the hydrophobic properties of the modified material was performed on the basis of the results obtained from the tests: water absorption, floating on the water surface and the contact angles were determined. Tests of the sorption of petroleum-derived compounds were performed on the basis of three procedures: in accordance with the technical sheet of the leading producer of hydrophobic sorption materials in Poland, the Westighouse's method in the oil layer and the Westighouse's method on a flat surface. The modified sorbent floats on the surface of the water very well. The average value of the contact angle for the modified sample is 104 degrees. Material is super hydrophobic. In the water environment, the hydrophobized samples have a higher absorption capacity in relation to oil contaminations compared to the raw material. Features of the modified sorbent, such as good buoyancy on the water surface, low affinity to water and better absorption of oil from the solution, make it possible to use the material to remove petroleum contamination from water and highly moist surfaces.

HYDROFOBIZACJA ZIEMI OKRZEMKOWEJ UŻYWANEJ DO USUWANIA ZANIECZYSZCZEŃ ROPOPOCHODNYCH

S ł o w a k l u c z o w e

hydrofobizacja, ziemia okrzemkowa, zanieczyszczenia olejowe

S t r e s z c z e n i e

Skażenie środowiska naturalnego zanieczyszczeniami ropopochodnymi jest nadal częstym i szczególnie niebezpiecznym zjawiskiem, dlatego usuwanie tych zanieczyszczeń jest konieczne. Różnego rodzaju sorbenty mineralne (minerały krzemianowe, zeolity, perlit, ziemia okrzemkowa, skały ilaste) ze względu na przystępną cenę, dużą selektywność i wysoką wydajność są wysoko cenione w procesach remediacji. Jednak wiele z tych sorbentów nie jest odpornych na wilgoć, co ogranicza ich zastosowanie. Proces hydrofobizacji poprawia efektywność sorbentów stosowanych w wilgotnym środowisku. DAMSORB produkowany przez IM-POL zhydrofobizowano metanolowym roztworem kwasu stearynowego. Użycie taniego kwasu stearynowego jako modyfikatora jest korzystne ekonomicznie. Ocenę właściwości hydrofobowych modyfikowanego materiału przeprowadzono na podstawie wyników uzyskanych z badań: nasiąkliwości, unoszenia się na powierzchni wody oraz wyznaczono kąty zwilżania. Badania sorpcji związków ropopochodnych przeprowadzono w oparciu o trzy procedury: zgodnie z kartą techniczną wiodącego producenta hydrofobowych materiałów sorpcyjnych w Polsce, metodą Westighouse'a w warstwie olejowej oraz na powierzchni płaskiej. Modyfikowany sorbent bardzo dobrze unosi się na powierzchni wody. Średnia wartość kąta zwilżania dla zmodyfikowanej próbki wynosi 104 stopnie. Materiał jest superhydrofobowy. W środowisku wodnym próbki hydrofobizowane mają większą chłonność w stosunku do zanieczyszczeń olejowych w porównaniu z surowcem. Cechy modyfikowanego sorbentu, takie jak: dobra wyporność na powierzchni wody, niskie powinowactwo do wody oraz lepsza absorpcja oleju z roztworu pozwalają na zastosowanie materiału do usuwania zanieczyszczeń ropopochodnych z wody i powierzchni silnie zawilgoconych.