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RESEARCH ON USING MINERAL SORBENTS FOR A SORPTION PROCESS IN THE ENVIRONMENT CONTAMINATED WITH PETROLEUM SUBSTANCES

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Abstract

A research on diatomite sorbents was carried out to investigate their ability to remove hazardous substances from oil spillages. We used two types of sorbents available on the market with differences in material density and particles size of composition. As sorbents we used Ekoterm oil and unleaded petrol 95 coming from refinery PKN Orlen S.A. Two types of sorbents with similar chemical composition but different granulometric composition were used. They are marked as D1 and C1 samples. The fastest absorbent was C1, but D1 sample was the most absorptive.

Keywords: sorbents, mineral sorbents, petroleum substances, sorption of chemical and ecological rescue

1. INTRODUCTION

In recent years, environmental protection and industrial pollution have become a number one issue. Poland as a member of the European Union must ratify international agreements in the field of environmental protection, particularly in the field of global warming and degradation of the natural environment. These facts force us to face a difficult task of establishing ways of preventing these processes. The main threat the environment and the humans are exposed to is pollution by petroleum substances. Danger is caused either by processing crude oil or exploiting or extracting oil, which chemically and physically is a toxic

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substance. A number of scientific researches are devoted to studying its production process, transport, convert and storage. Risks of pollution related to oil use are huge as faults occur frequently. It is absolutely necessary to discover a new, alternative source of energy which will be more environmentally friendly. However, alternative sources haven't been adopted by the global market and still processed oil substances remain a major source of car fuel and heating energy. They create a direct danger during production process, transport, conversion and storage. Accidents occur infrequently, but the consequences are devastating. Thus they must be considered as the accidents with high risk rate. Most of the dangerous accidents take place during transportation. Emergency situations can also take place on oil rigs, although it is terare. It is worth emphasizing that considering the volume of produced medium, this can have catastrophic character. First minutes after contamination are most important and that is why time of reaction is very important in this kind of situations. The quick action has to be taken to isolate substances from environment [1].

Rescue teams use specialistic equipments such as peristaltic pump, barrel pump, membrane pump, oil barrier, oil separator etc. for quick collection of the substance. These devices have an adequate chemical resistance and are useful for the areas where the accumulated amount of the substance is large [2].

However, the problem make cases, when a liquid substance is not possible to be recovered by mechanical equipment for many reasons. In order to reduce the effects of either great disaster or small leakage, in the last stage of cleaning of the ground a porous sorbents or dispersants are applied [2].

These sorbents are solid materials (in the form of granular, mats, cushion, sorption barrier, etc.) used to reduce the migration of the substances horizontally and vertically. The most frequently used sorbents are the sorbents of the mineral origin. Because of the specific structure and absorption properties sorbents seems to be very effective [3].

Poland is a country rich in natural mineral sources. In general, they are clayey rocks, siliceous and others, which after slight modification are ideal for sorption processes. They have a wide range of application in industry, agriculture and environmental protection, what shows their versatility. In terms of the sorption properties special interest deserves a group of silicate minerals such as SiO_2 diatomite, diatomaceous ground and silica. Their geological composition includes mainly chalcedon and opal, as well as other minerals such as: quartz, stobalit, clay minerals and carbonates. Opal is commonly used as a sorbent material. It is an amorphous mineral consisting of $[SiO_4]^{-4}$ anions in tetrahedral arrangement, creating a skeleton containing water molecules. Moisture content can be controlled during the drying process. In normal conditions, it may crystallize. These crystals are called chalcedony - a semi-crystallized form variety of quartz [4]. The properties of this type of sorbents are result of improved active surface area, porosity and presence of hydroxyl group - OH, sometimes also called silanol. This group is created either in the process of condensation of monomers during the opal synthesis or when monomers are in contact with other substances [4]. "Geological form of diatom is called diatomite (diatomaceous earth filter or slates) 1 cm^3 contain around 2,5 billions of diatoms", and the eldest are dated for 400 million years ago" (Fig. 1) [5].

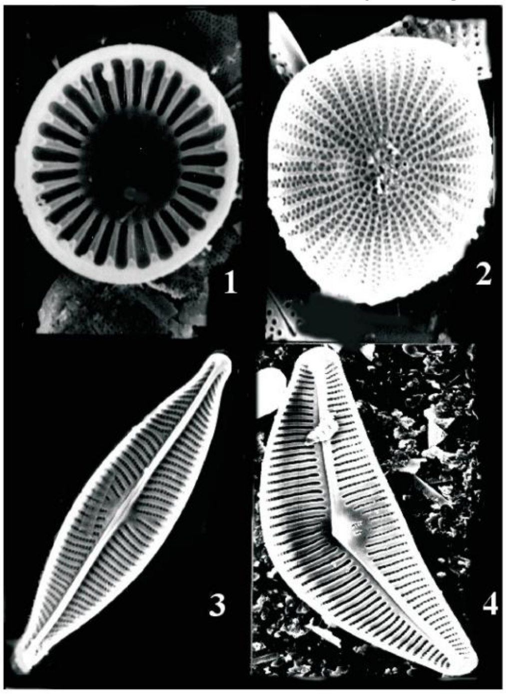

Fig. 1. Diatomite in electron microscope: 1 - *Cyclotella meneghinina* zoom 6000x, 2 - *Stephanodiscus hantzschii* zoom 9400x, 3 - *Navicula rynchotella* zoom 4400x, 4 - *Cymbella cistula* zoom 3000 [3].

Chemical composition of debris is presented in Table 1.

Table 1. The percentage of substances in contaminated diatomite [2]

No.	Substance	Content [%]
1.	SiO_2	65 - 80
2.	Al_2O_3	5 - 10
3.	Fe_2O_3	0.5 - 4

Diatomite activation with base or acid and base causes an improvement in adsorption ability. This effect can be reached as well with thermal treatment, but performed in relatively low temperatures (150-400 ºC). High temperature causes an opposite effect [4].

2. RESEARCH

2.1. The physic-chemical properties of sorbents and sorbants used in this research

We used diatomite coming from two commercial sources (D1 and C2). The physic-chemical properties are shown in table 2.

Table 2. Comparative characteristics of sorbents

No.		Sorbent D1	Sorbent C2
1.	Identification		
		Granulated and calcined	Granulated and calcined diatomaceous soil
2.	Chemical composition		
	SiO_2	75.00 %	75.00 %
	Al_2O_3	10.00 %	10.00 %
	Fe_2O_3	7.00 %	7.00 %
	TiO_2	1.00 %	1.00 %
	MgO	2.00 %	2.00 %
	CaO	1.00 %	1.00 %
	$K_2O + Na_2O$	2.00 %	2.00 %
3.	Form		
		Granulate 0.5 - 2.00 [mm]	Granulate 0.3 - 0.7 [mm]
4.	pH		
		5,5	5,5
5.	Density		
		509.00 [g/dm^3]	532.00 [g/dm^3]
6.	Colour		
		Red - brown	Brown

The highest percent have the particles with the diameter of 1,2 mm and next come those having the size of 2.00 mm and 0.6 mm. For sample C2 these data hasn't been provided. Difference can be observed in the colour of the samples. C2 has metallic shinning of small particles.

As a sorbates we used unleaded petrol 95octane and Ekoterm Plus heating oil, which is similar in properties to fuel oil. Both are provided from refinery PKN Orlen S.A., reason for choosing this substance is that they are often involved in accidents causing danger for environment. Characterization of unleaded petrol 95 octane and Ekoterm Plus oil is presented in table 3 and 4 [8], [9].

Table 3. Chemical and physical data of heating oil and unleaded petrol 95.

Ekoterm Plus		
No.	Data	Number
1.	Appearance	Red liquid
2.	Smell	Characteristic of diesel and heating fuel
3.	The pH value	not relevant
4.	Melting and boiling range	180ºC - 360ºC
5.	Flash point	> 56ºC
6.	Vapour pressure at 50°C	2kPa
7.	Relative density at 15°C	0.86 g/cm^3
8.	Ignition temperature	≥ 270ºC
9.	Kinematic viscosity	6 mm^2/s
Unleaded petrol 95		
No.	Data	Number
1.	Appearance	Yellow liquid
2.	Smell	Characteristic of petrol
3.	The pH value	not applicable
4.	Melting and boiling range	From 30ºC to 210ºC
5.	Flash point	- 51ºC
6.	Vapour pressure at 50°C	118,6 kPa
7.	Relative density at 15°C	0.720 - 0.775 g/cm^3
8.	Ignition temperature	≥ 340ºC
9.	Ignition temperature	6 mm^2/s

2.2. Methodology

Aim of this study was to analysis the process of adsorption in time and presentation of down-stream regulation of this action. Experiment was simulating the real accident of oil release to environment.

Scaling was including four steps. Weight of component listed below had to be known. Before setting weight should weigh and recorded mass values:

1. bucket,
2. PET container,
3. 150 ml of sorbate,
4. As a last we weight 50g of sorbent - our object of research (SD 0,10g).

Bucket with sorbent was hung under arm of scales, next PET bucket with chosen oil was placed under previous bucket. Reaction time was counted from the moment of pouring sorbent into bucket with oil and weight changes were reported every 30 seconds.

Process of adsorption is terminated when scales do not register any changes in weight. Records included final time of adsorption, weight of sorbent after experiment and weight of remaining oil substance in PET bucket. Final data was obtained by subtracting the weight of crude sorbent from weight of the sorbent after the process.

2.3. Research working place

Main element of research working place was an electronic scale with standard deviation of 0,001 gram. Scale was permanently screwed to laboratory bench. On the scale there were fit two blades, each of 25 cm long, wherein one of them was located under the scales. Two of them were combined by means of threaded pins Ø 5 [mm]. In the bottom part, under the scales, the cage was fixed to the blade by flexible metal hose. It applied a bucket (size: height 100 [mm], diameter 55 [mm] and aperture size 0,5 [mm]). Under bucket was located an open tray PET, which was set on regulated stand. Regulated stand was used to lift free surface liquid during its falling down. All of this is assembly under a fume cupboard.
Saturation ratio can be calculated from the formula:

$$sorption[S] = \frac{mass\ sorbate[m_{te}]}{mass\ sorbent[m_t]}\left[\frac{g}{g}\right] \tag{1}$$

where:
mass sorbent [g] = gross mass sorption system [g] - mass of clean sorbent [g] - mass of bucket after sorption process[g].

The percentage of sorbent absorptiveness can be count to multiple S and 100 %

$$S\% = S \cdot 100\% \tag{2}$$

value. (form. 2).

Conditions for the experiment were 18 ºC and 101 305 Pa of atmospheric pressure. In first part of experiment only one repeat has been carried out for each sample (D1 and C2) and as a sorbent Ekoterm Plus was used.

3. RESULTS

Analysis of D1 and C2 ability to adsorb Ekoterm Plus suggests higher rate of speed for sample C2. We hypothesize that the obtained differences are caused by physical properties of the sorbent i.e. number of smaller and bigger particles per volume unit. Chemical composition of these two samples is the same. In both cases, whole volume of sorbat took part in process of adsorption. This means that Van der Waals forces between molecules of sorbent and sorbat are stronger than gravity. The level of sorbent D1 and C2 saturation, based on from Fig. 2 was 1.05 and 1.00, respectively.

Ability to suck the sorbat counted in percentage remain 105.43% and 100.42% from D1 and C2, respectively.

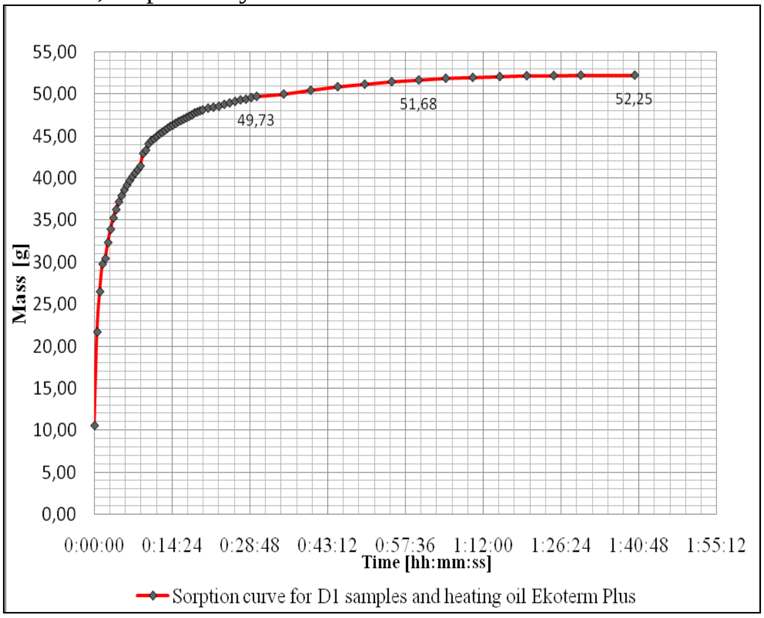

Fig. 2. Graph of sorption in time D1 sorbent and Ekoterm Plus oil term

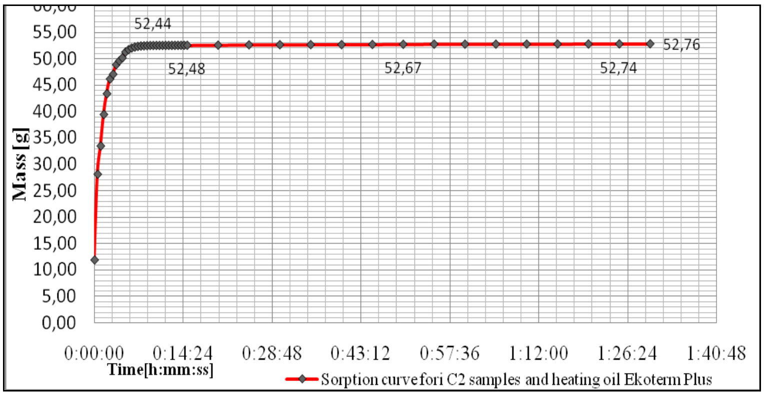

Fig. 3. Graph of sorption in time C2 sorbent and Ekoterm Plus oil term

In the second part of the research a different sorbat was used - Unleaded petrol 95. Analysing data from Fig. 3 and 4 we can observe that adsorption is spontaneous and occurs in relatively short time. And once again C2 sample is having higher rate of speed. Ability to suck the sorbat counted in percentage remains 98% and 94% from D1 and C2, respectively.

Average difference in level of sucking properties in both experiments is around 4-5% and D1 has greater properties. We suggest that it is caused by different sized particles composition and improved number of macro-and - mesoporosity.
Speed rate for C2 in both experiments is greater comparing to D1. Time of absorption for unleaded petrol 95 was shorter than for the other sorbat and was from 0' to 3 minutes.
Result can be expressed in time rate per volume unit. (Fig. 5.)

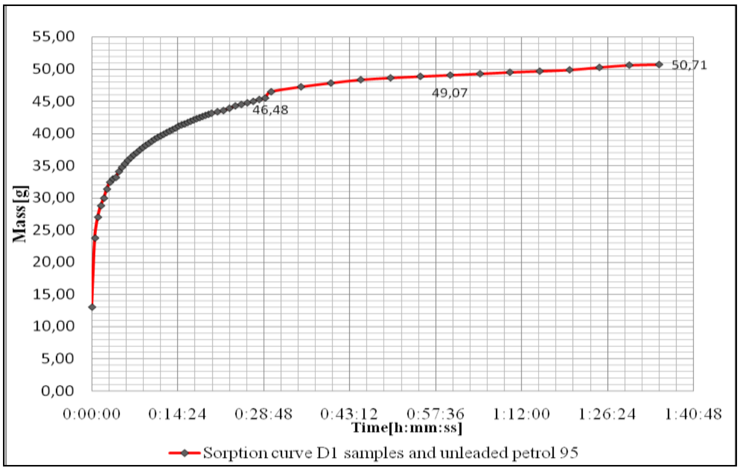

Fig. 4. Graph of sorption in time D1 sorbent and unleaded petrol 95 octane

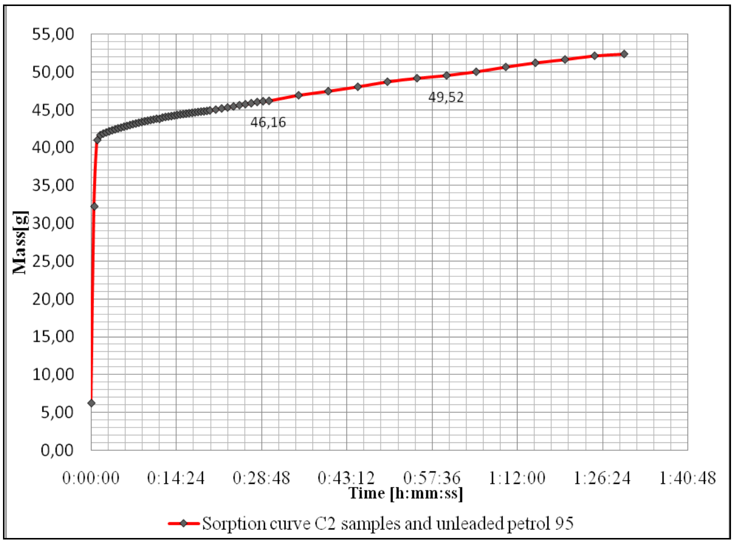

Fig. 5. Graph of sorption in time C2 sorbent and unleaded petrol 95 octane

4. DISSCUSSION AND CONCLUSION

Data analysis suggests that better adsorption can be provided by mineral D1 sample. Greater adsorption was observed either in the first or in the second trial. These results are probably caused by the size of the particles and their content in the whole composition. D1 possesses a higher percentage of molecules in size above 1mm. It is connected with bigger number of macro- and mesoporous porosity, which is much lower in C2 sample.

C2 sample had a better result in time rate of adsorption. This spontaneous process took place in relatively short time and sorbent change in colour had been observed

This research suggests a higher efficiency of sorbent D1 in general, but if the time rate is important criteria C2 sorbent should be used. The result of this study will be helpful for chemical-ecological emergency team when an accident occurs. Sample D1 should be used in case, where pollution needs to be fully removed from environment and time limit doesn't play a role. This sorbent can be used to secure catch - basin grate. When the time is the limiting factor, for example in danger of fire, C2 sorbent will be a better choose.

Adsorbents which have been used in the study are less adsorptive than synthetic sorbents e.g. porous polyurethane foams [10], which have uptake capacity 20. However their mass is higher than the mass of synthetic sorbents, and can be used in windy days. Sorbents from diatomite are in 100 % natural and unlike the synthetic sorbents [11] do not produce harmful product of combustion. The adsorbents used in the study are ideal for use on impervious hardened surfaces. Additionally, speed rate of adsorption process is strictly dependent on density of our chosen sorbent.

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BADANIE PROCESU SORPCJI SKAŻEŃ ŚRODOWISKA SUBSTANCJAMI ROPOPOCHODNYMI Z WYKORZYSTANIEM SORBENTÓW MINERALNYCH

Streszczenie

Przeprowadzono badania nad sorbentami pochodzenia okrzemkowego diatomitowego, stosowanymi do usuwania substancji niebezpiecznych, przy awaryjnych wyciekach. W badaniach zastosowano dwa rodzaje sorbentów dostępnych na rynku, różniących się gęstością nasypową i składem granulometrycznym. Scharakteryzowano diatomity pod względem mineralogicznym, sorpcyjnym i występowania geologicznego w Polsce. Jako sorbatów użyto oleju opałowego Ekoterm Plus i benzyny bezołowiowej 95 z rafinerii PKN Orlen S.A. Podczas badań wykazano, że sorbenty o niższym składzie granulometryczym i większej gęstości nasypowej, wykazują większe właściwości sorpcyjne. Zarówno w pierwszej części jak i drugiej części badania, najszybciej chłonącym sorbentem okazał się C2, natomiast bardziej chłonnym (pod względem objętościowym) okazał się sorbent D1. Diatomity są dobrymi sorbentami pochodzenia organicznego, które spełniają oczekiwania pod względem sorpcyjnym. Swoje pochodzenie zawdzięczają mikronowym obumarłym komórkom glonowym. Ich atutem jest wielofunkcyjność zastosowania zarówno w ochronie środowiska, rolnictwie czy też przemyśle ciężkim.

Słowa kluczowe: sorbenty, sorbenty mineralne, substancje ropopochodne

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