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Use of diatomite from Polish fields in sustainable development as a sorbent for petroleum substances

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ABSTRACT

Diatomites are one of the most interesting materials found in various regions of the world. In Poland, there is the only active diatomite mine in Jawornik Ruski in the Podkarpacie region. Diatomite fields in Poland with an average SiO2 content of 72% are found in the Carpathian Mountains, in the Leszczawka region. Geological data indicate the existence of at least 4 large deposits of this material, but one deposit (Jawornik) is being exploited. The diatomite from the Polish deposit differs from other raw materials of similar origin. It has recently been the subject of intensive scientific research aimed at its extensive use in industry, breeding, and agriculture. This locally occurring material has different properties from other such materials existing in other regions, which is why its research is important in terms of its potential use. The balance resources are estimated at about 10 million tons, so its economic use can have an impact not only locally but globally. In spite of the different chemical and phase composition in relation to competing diatomites, it was hypothesized that it would be possible to select appropriate processing parameters on the basis of a series of investigations into the properties, so that even from the raw material of not the best quality, products could be obtained which were superior to those of competitors in terms of sorption parameters. In the presented research we used, among other things, the Westinghouse method to determine the degree of absorption of diatomite, as well as such research methods as particle size analysis, X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM). Specific surface area measurements were determined using the single-point and multi-point Brunauer-Emmett-Teller (BET) methods. Results of physicochemical analyses of diatomite and results of absorption of petroleum substances are presented in the article. As a result of the research, it was found that diatomite of Polish origin may have an absorption capacity of oil derivatives at the level of about 130% by weight. This result is of great commercial importance because the degree of absorption is superior to other competing materials. This material can be successfully used to remove various oil spills and eliminate environmental hazards. The results of the investigations are also of economic importance, as the production of the best quality sorbents from locally available raw materials reduces transport costs and thus the environmental impact. In addition, the production of highly efficient sorbents reduces the consumption of raw materials as well as the waste of sorbents impregnated with petroleum-derived substances. It is estimated that the savings from producing sorbents with the parameters described in the article will be about 30% in comparison to popular competitive materials of other origins.

1. Introduction

Diatomites are rocks formed by the transformation of diatom shells. These materials stand out for their interesting properties and many applications. Examples of applications include: a sorbent for absorbing petroleum substances, an additive for concrete, a parasite control agent for poultry farming, an agent used in beer filtration, an additive for paints and varnishes, and plastics, a carrier for pesticides, and others. In

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many applications, diatomite plays the role of a mere filler, however, due to its properties, it can also be an active additive, performing certain functions. Its properties related to stopping idiogeopathic radiation of the earth have also been confirmed.

Diatomite deposits in Poland are located in the Podkarpackie Voivodeship and the only active deposit is in Jawornik Ruski. The company, which has been mining the resource for more than 40 years, has noticed an increase in interest in diatomite from many industries in recent periods. In Poland, diatomite extraction in 2021, according to data from the "Balance of mineral resources in Poland as at 31 December 2021". (Bońda, 2022), oscillated around 0.98 thousand tons. Due to the shortage of diatomite raw materials in the Polish domestic arena, imports of these substances have been growing dynamically for years, customarily from the USA and Denmark, and increasingly from Germany and Mexico. According to published data (Crangle, 2022), US diatomite exports to various countries around the world in 2021 amounted to 830,000 tonnes, with an estimated value of US\$274 million. The value of diatomite in 2021 varied widely, ranging from around US\$10 per tonne (lightweight construction aggregate) to more than US\$1000 per tonne (cosmetology, medicine). However, the final price of the material is also dependent on one factor, namely the exchange rate. According to Vochozka et al., 2020a,b; 2020) the exchange rate of the above currencies can be attributed to fluctuations in oil prices, which can largely affect the value of the euro and the dollar in any given year. The US is the world's leading producer of diatomaceous earth. Despite the disruption caused by the global COVID-19 pandemic, US diatomite production through 2021 remains at about the same level as in 2020. Therefore, a number of scientific research and development initiatives have been undertaken to understand all the properties of locally occurring diatomite in Poland and develop processing technologies to create advanced functional materials.

Most raw materials of this type on the Polish market are used in filtration and purification processes in the chemical and food industries (e.g., in the beer filtration process). Diatomite raw materials are also used in the production of insulation and soundproofing materials. A quite common use of granules is as a sorbent for petroleum substances in various types of emergency spills (at gas stations, airport runways, factory floors, and in the case of water spills, etc.), as well as in agriculture as a carrier for pesticides and in zoology as a bedding for pets.

Diatomites and diatomaceous earth are widely used as filtration materials, sorbents, movers for pesticides, catalysts, thermal insulation, as well as, polishing materials However, typical diatomites with SiO_2 content above 80% do not occur in Poland (Bońda, 2021a,b).

Documented balance resources of diatomite rock are around 10 million tons. Fig. 1 shows the diatomite deposits located in Poland in the Podkarpackie Voivodeship.

Diatomite has become very popular among consumers, as systematic consumption of diatomaceous earth has been shown to reduce levels of



Fig. 1. Location of the diatomite mine in Poland in the Podkarpackie Voivodeship, and diatomite mine overview photo.

unfavorable cholesterol (LDL) and triglycerides in the recent year. Moreover, the beneficial impact of silicon on bone and connective tissue was demonstrated (Szymańska and Kręgiel, 2021).

Diatomite raw materials can also be used in the synthesis of zeolites and sorbents. As studies (Grela et al., 2016, 2021, 2016a; Łach et al., 2018, 2019ach et al., 2019a) have shown, it is possible to produce complex zeolite structures from various types of waste raw materials containing significant SiO₂ content. The possibility of obtaining Y-type zeolites from diatomites has been confirmed (Garcia et al., 2016) as well as zeolites obtained by the method using microwaves (Stafin et al., 2021).

High-temperature investigations of clayey (loamy) diatomite have indicated that heat processing at 1000 °C causes the forming of a mullite a typical for this temperature. Nevertheless, its presence is attributed to the high reactivity of the diatomite clay (the presence of an amorphous phase and superfine particles). The temperature increase to 1200 °C, resulted in a significant rise in the mullite phase with a concomitant rise in the amorphous phase and the appearance of tridymite. According to the obtained results, diatomite clay was found to have the potential to be used at much lower temperatures as a basic raw material for the preparation of various ceramic materials (structural and thermal insulating elements), zeolites of various types, water glass, amorphous SiO₂, etc. The reason for this is the presence of mullite as a component of the binder, allowing for high mechanical properties (Reka et al., 2020).

Diatomite can also be used as a carrier for phase change materials (PCM) (Dong, 2017; Karaman et al., 2011; Xu and Li, 2013). In another work (Qian et al., 2015), lithium nitrate (LiNO₃), polyethylene glycol (PEG), and sodium sulfate (Na₂SO₄) were used as a storage medium, which was then mixed with diatomite by vacuum impregnation or by blending and sintering, as appropriate. Their maximum charges of PEG, LiNO₃, and Na₂SO₄ in diatomite powder achieve 58%, 60%, and 65%, respectively. XRD, FT-IR and SEM results showed that the PCMs were well dispersed in the pores of the diatomite and were quite stable thermally and chemically even after 200 cycles of melting and freezing. Other authors also confirmed the usefulness of diatomite for the production of composites with phase change materials, or the good quality of the diatomite combination with paraffins was confirmed. Among them, some authors (Benayache et al., 2018) presented a study of impregnation of the raw and the calcined Algerian diatomite with a mixture of liquid paraffin and paraffin to obtain composite PCMs. They proved that the produced materials are suitable for thermal energy storage in buildings. Studies by other researchers (Xu et al., 2017) present the possibility of using diatomite to form a stabilizing sodium nitrate. The produced PCM composites have high efficiency in thermal cycles and are used in medium-temperature thermal energy storage. Researchers from Soongsil University (Jeong et al., 2013) created PCM/diatomite composites by introducing PCM in the form of paraffin wax, n-hexadecane and n-octadecane into the pores of diatomaceous earth. PCM/diatomite composites can contribute to energy savings by increasing thermal efficiency due to the accumulation of latent heat. Other authors (Miliozzi et al., 2019) in their work presented the possibility of producing novel cementitious mortars through mixing the basis mortar with, among other things, phase change materials. They proved that PCM and the diatomite compound increase conductivity and volumetric thermal capacity.

The authors of the work (Chaisena and Rangsriwatananon, 2004) examined a sample of diatomite (diatomaceous earth) from northern Thailand. In its natural state, this material was a poorly-ordered opal A type with a small amount of quartz. Calcination at high temperatures up to 1100 °C showed that the diatomite particle size distribution decreased as the temperature increased. Similar to other studies (Van Garderen et al., 2011; Zheng et al., 2018), the authors of the present study found the presence of cristobalite after calcination at 1100 °C. Research involving measurements of diatomite dissolution in sulfuric acid after various thermal treatments has been carried out. The samples were calcined at 900, 1000 and 1100 °C and then treated with 6M H₂SO₄; 6M

HCl and 6M HNO_3 at about 100 $^\circ\text{C}.$

The authors of the work (Reka et al., 2021) conducted the study of raw diatomite from North Macedonia Their research revealed silica phase transitions and phase transformations occurring throughout the calcination process. An amorphous opal was transformed into cristobalite during the calcination process. The most significant changes were noticed in the temperature range of 1000–1100 °C. At 1100 °C, all opal was completely transformed into cristobalite. In the temperature range of 1100–1200 °C, transformation of cristobalite into mullite was observed. As a result of the research, it was found that apart from the known sorption and filtration properties resulting from the presence of diatoms and channels with nanometric structures, the material is appropriate for the formation of variety of ceramic materials (Reka et al., 2021).

The diatomite research (Celite 499, Celite Korea Co. Ltd., Korea) (Ha et al., 2013) was used to prepare sintered filters. As a result of the research, it was found that diatomites can be used in the form of diatomite sinters as porous ceramics for membrane microfiltration (Ha et al., 2013). Tests conducted on diatomite earth samples from Shengzhou County (Zhejiang, China) revealed that in fact, diatomite has significant application potentially for economically removing Co(II) from contaminated wastewater (Sheng et al., 2012).

There are also attempts to use diatomite as an additive to concrete and cement binders (Ergün, 2011; Lv et al., 2022; Sun et al., 2020). The research carried out with the use of diatomite from Poland (Kapeluszna et al., 2021) allowed for the conclusion that diatomite11increases the demand for water. The addition of diatomite reduces the consistency of fresh concrete mix both after 5 min and 40 min after mixing. The early strength of the diatomite-modified mortars is lower than that of the reference samples. However, after 28 days of seasoning, this strength increases, which may indicate the pozzolana nature of this material (Kapeluszna et al., 2021).

This article presents a short description of diatomite from deposits in Poland, as well as the possibilities of using it as a sorbent for petroleum substances.

The results of the research carried out are of great importance because the use of such a raw material will contribute to a number of environmental and economic benefits. Because at present, Poland imports very large amounts of raw material, including from the USA, Mexico and Denmark, the possibility of using their domestic material is much more advantageous. This raw material, offered as a sorbent for petroleum substances, will be much more available and will have a greater absorption capacity (by weight). The subject of the research relates directly to the field related to environmental protection, cleaning of areas from petroleum substances, etc.

The research results presented in this paper are undoubtedly a novelty, taking into account the raw material they concern. So far, despite the existence of a diatomite mine in Poland since the 1970s, such comprehensive research has not been carried out. It should also be noted that Poland has one of the largest deposits in Europe of this raw material. The approach and research results presented in this paper are new, taking into account the type of raw material tested. Diatomite from Poland is a specific material and differs significantly from other diatomites or diatomaceous earth of other origin.

Due to a number of still unrecognized properties of locally occurring diatomite, it is planned to initiate advanced research aimed at using diatomite as a bactericidal and fungicidal additive for paints, varnishes and other coatings, as well as an agent used in agriculture. Since diatomite is a proven additive against, for example, the external poultry parasite "bird fluke," it is planned to expand research related to its fungicidal and bactericidal properties as well. It is planned to conduct microbiological tests using standard strains of mold fungi and bacterial strains from the ATCC collection. In agricultural applications, there is also a high probability of suitability of diatomite (also after its surface modification) for use as a carrier of N, P, K nutrients.

2. Materials

The research material is diatomite from the Polish deposit located in Jawornik Ruski in the Podkarpackie Voivodeship (producer: Górtech Sp. z o.o, Cracow, Poland). An example of the appearance of diatomite aggregate is shown in Fig. 2. Raw diatomite and calcined diatomite were tested to determine the effect of thermal treatment on its properties. After the calcination treatment, the diatomite was granulated in a drum granulator Due to its use as a sorbent used on roads (collision sites) and in other facilities where there is leakage of petroleum substances, an aggregate or granular form is required (with the amount of dust up to 10-15%).

3. Experimental investigations and results

3.1. Morphology investigations

The morphology of the diatomite has been observed using a scanning electron microscope JEOL IT200 (JEOL, Tokyo, Japan, 2021). The raw material, before thermal treatment, was thoroughly examined, as regards the physico-chemical properties. First of all, detailed observations of the particle morphology of various fractions of diatomite in the raw state were made using a scanning electron microscope as well as chemical composition analysis. The exemplary photographs of diatomite particles are shown in Fig. 3. The remains of diatoms in various forms are there clearly visible. Further observations were carried out in terms of changes in the structure of mainly these diatom fractions.

Fig. 4 presents the scanning electron microscope images of diatomite after heat treatment at a temperature of 850 $^\circ$ C.

Fig. 5 presents the scanning electron microscope images of diatomite after heat treatment at a temperature of 1160 °C. The appearance of the liquid phase and melting of the diatomite particles can be seen. The applied temperature is too high and destruction of diatomite skeletons (shown in Fig. 3) and other minerals occurring in diatomite takes place. This is important due to the fact that manufacturers of diatomite sorbents from other regions of the world specify the calcination temperature as 1160 °C. In the case of diatomite of Polish origin, this temperature is too high, as evidenced just by Fig. 5.

3.2. Laser particle size analysis

The particle size characteristics were performed via the particle size analyzer Anton-Paar PSA 1190LD (Anton-Paar, Graz, Austria, 2021). Particle size analyses were carried out for diatomite in dust form. The distribution of particle size is shown in Fig. 6, while the particle size



Fig. 2. Non-calcined diatomite aggregates.



Fig. 3. Morphology of diatomite particles (without thermal treatment).



Fig. 4. Calcined granulated diatomite.



Fig. 5. SEM micrograph of diatomite after heat treatment at 1160 $^\circ\text{C}.$

parameters are summarized in Table 1.

3.3. Examination of chemical composition

The chemical composition of the diatomite was tested on the PAN-alytical Epsilon $3^{\rm XLE}$ X-ray fluorescence spectrometer. Ignition losses



Fig. 6. Distribution of diatomite particle size.

Table 1

Particle size data of analyzed diatomite.

Parameter	Unit	Result
D ₁₀ D ₅₀	μm	$\begin{array}{c} 2.885 \pm 0.036 \\ 10.955 \pm 0.203 \end{array}$
D ₉₀ Mean size		$\begin{array}{c} 22.103 \pm 0.361 \\ 12.417 \pm 0.203 \end{array}$
Span	-	1.754 ± 0.004

were calculated according to the PN-EN 1744-1 + A1: 2013-05 standard. Chemical composition analysis results are shown in Table 2.

3.4. Mineralogical analysis

The mineralogical composition of diatomite was investigated by means of an X-ray diffraction technique using a PANalytical Aeris (Malvern Panalytical, Almelo, Netherlands, 2016) diffractometer. Diffractograms were recorded using Cu-K α radiation in the scan range of 10–70°2 θ , and with a step size of 0.003°(2 θ). Qualitative analysis of diatomite was carried out using the Rietveld method. Patterns of X-ray diffraction of raw diatomite and calcined diatomite are shown in Fig. 7.

Table 2

The chemical composition of diatomite determined by X-ray fluorescence analysis.

Component	Concentration	Unit
SiO ₂	68.52	%
TiO ₂	0.52	
Al ₂ O ₃	11.78	
Fe ₂ O ₃	4.65	
MnO	0.04	
MgO	0.83	
CaO	0.38	
Na ₂ O	0.34	
K ₂ O	2.29	
P ₂ O ₅	< 0.01	
SO ₃	0.59	
SrO	0.01	
Cl ⁻	<0.01	
v	112	ppm
As	9	
Rb	108	
Zr	101	
Y	22	
Cu	56	
Pb	34	
Ba	122	
Ni	40	
Cr	92	
Zn	72	
Ga	15	
LOI	9.97	%

In addition, the results of quantitative analysis are summarized in Table 3.

3.5. Investigations of specific surface area, pore volume and pore diameter

The tests of specific surface area, pore volume and pore diameter were carried out using a Quantachrome Autosorb iQ-MP physical sorption analyzer (Anton Paar, Graz, Austria, 2016). The sample degassing process was carried out in several stages: 1) heating to the degassing temperature of 80 °C at the rate of 2 °C/min with soaking time of 30 min; 2) heating to 120 °C at the rate of 2 °C/min and soaking for 30 min; 3) heating to degassing temperature of 350 $^{\circ}$ C at the rate of 5 $^{\circ}$ C/ min and soaking time of 300 min. Specific surface area measurements were determined using the single-point and multi-point Brunauer-Emmett-Teller (BET) methods. The volume and diameter of pores were determined by the BJH method (Barrett-Joyner-Halenda). The microporosity of the samples was determined using the Dubinin-Raduszkiewicz (DR) method. The results were analyzed with Quantachrome ASiQwin software. Fig. 8 presents nitrogen adsorptiondesorption isotherms of crude diatomite and calcined diatomite at 750 °C.

3.6. Determination of porosity

The diatomite porosity was tested using a mercury intrusion pore size analyzer (Quantachrome PoreMaster 33). The pressure range of this device is 0.2–50 psi (low pressure range) and 20–33 000 psi (high pressure range). The range of measured pore sizes is 6.4 nm–1100 μ m. The results for pore volume and pore size and specific surface area of the diatomite are shown in Table 4.

3.7. Differential thermal analysis

Differential thermal analysis (DTA), coupled with thermogravimetry (TG) was performed with NETZSCH STA 409 C/CD instrument (Netzsch GmBH, Selb, Germany). The samples were heated at 10 °C/min he tests were conducted in an argon atmosphere in the temperature range from 30 °C to 1000 °C. Comprehensive testing on an advanced thermal analyzer was aimed at selecting the optimum calcination temperature. Fig. 9 presents a diagram of the thermal analysis showing the changes occurring in the material (heating effects).

3.8. Radioactivity investigations

The concentrations of naturally radioactive elements (⁴ K, ²²⁶Ra, ²²⁸Th) in diatomite were examined using multi-channel analyzer PI-MAZAR 01 (POLON-IZOT, Warsaw, Poland) with the gamma exposure dose of 77,58 μ Gy/h. The measurement time was 30 cycles of 2.000 s, whereas the sample weight was 975 g. In accordance with effective legal regulations, i.e., the regulation of the Council of Ministers, in the case of "requirements regarding the content of natural radioactive isotopes in raw materials and materials used in buildings for human and livestock habitation, as well as in industrial waste used in construction, and the control of the content of these isotopes", building materials are qualified based on two activity indicators, determined in accordance with the following relationships (Lach et al., 2019b; Marczyk et al., 2021):

$$f_1 = \frac{C_{K-40}}{3000 \ Bq \ kg^{-1}} + \frac{C_{Ra-226}}{300 \ Bq \ kg^{-1}} + \frac{C_{Th-228}}{200 \ Bq \ kg^{-1}}$$
(1)

$$f_2 = C_{Ra-226} Bq kg^{-1}$$
 (2)

where: C_{K-40} , C_{Ra-226} and C_{Th-228} are the isotope concentrations of potassium ⁴ K, radium ²²⁶Ra and thorium ²²⁸Th, expressed in Bq kg⁻¹. Table 5 details the natural radioactivity concentrations of ⁴ K, ²²⁶Ra, and



Fig. 7. X-ray diffraction (XRD) patterns of both forms of diatomite: without treatment and after calcination process carried out at 750 °C.

 Table 3

 The results of quantitative analysis performed for diatomite before and after heat treatment.

Type of diatomite	Quantitative share of phase [%]			
	Silicon Aluminum Oxide Oxide		Kaolinite	Albite
	SiO ₂	Al ₂ O ₃	Al ₂ Si ₂ O ₅ (OH) ₄	NaAlSi ₃ O ₈
Diatomite before treatment	32.9	0.4	48.5	18.2
Calcined diatomite	37.7	0.2	31.2	30.9



Fig. 8. Adsorption-desorption isotherms of nitrogen for raw diatomite and calcined diatomite at 750 $^\circ\text{C}.$

 ^{232}Th in the analyzed diatomite. From the measured concentrations of radionuclide activity, the f_1 and f_2 coefficients were calculated.

3.9. Absorption capacity

The absorption capacity of the agglomerate relative to petroleum derivatives was examined by the Westinghouse method, in accordance with the annexe to the regulation of the Minister of Interior and Administration of 20 June 2007 on the list of products used to ensure public safety or protection of health and life and property, as well as the rules for issuing admittance for use of these products (Journal of Laws No. 143, item 1002), introduced by the amending regulation of April 27, 2010. (Journal of Laws No. 85, item 553 p. 9.1.2.1.). The tests were conducted with diesel fuel meeting the requirements of Polish standard PN-EN 590 for diesel fuel grades for temperate climates. Fig. 10 shows the results of oil absoption tests for different diatomite variants.

Furthermore, in the next step the absorbency of the diatomite was tested (Fig. 11), depending on the applied treatment with aggressive agents, such as 5M solution sodium hydroxide (5M NaOH), hydrochloric acid (HCl), 3% solution of hydrochloric acid (3% HCl), sulfuric acid (VI) (H₂SO₄), and 3% solution of sulfuric acid (VI) (3% H₂SO₄). Moreover, raw diatomite without chemical treatment was used as reference material.

4. Discussion

The raw material, before thermal treatment, was thoroughly examined, as regards the physico-chemical properties. First of all, detailed observations of the particle morphology of various fractions of diatomite in the raw state were made using a scanning electron microscope as well as chemical composition analysis. The exemplary photo-graphs of diatomite particles are shown in Fig. 3. The remains of diatoms in various forms are there clearly visible. Further observations were carried

Table 4

Textural characteristics of diatomite.

Sample No.	Specific Surface Area [m ² /g]		Pore Volume [cm ³ /g]			Pore Size [nm]	
	BET Surface Area (Single Point)	BET Surface Area (Multi Point)	Total Pore Volume P/ $P_0 = 0.99$	BJH Pore Volume	DR Pore Volume	BJH Average Pore Diameter	DR Average Pore Diameter
Raw diatomite	25.273	27.373	0.06585	0.06422	0.01062	1.511	2.021
Calcined diatomite	12.223	13.055	0.05878	0.05835	0.00505	3.415	2.079



Fig. 9. Thermal decomposition of the diatomite during heating from ambient temperature to 1000 °C: thermogravimetry (TG) and differential thermal analysis (DTA) curves.

Table 5	
Natural radioactivity concentrations of ⁴ K,	²²⁶ Ra, ²³² Th of the tested material.

Radioisotope	Unit	The radioactivity concentrations
Potassium, ⁴ K Radium, ²²⁶ Ra Thorium, ²³² Th	Bq kg ⁻¹	$\begin{array}{l} 477.27 \pm 45.14 \\ 67.77 \pm 8.87 \\ 41.52 \pm 5.12 \end{array}$

out in terms of changes in the structure of mainly these diatom fractions. Fig. 5 presents the scanning electron microscope images of diatomite after heat treatment at a temperature of 1160 °C. Comparing the SEM micrographs of the processed diatomite to the SEM images of the diatomite particles without thermal treatment presented in Fig. 3, it can be observed that the diatomite powder was partially melted at 1160 °C. This leads to the closure of the internal porous structure of the diatomite powder. Such dependencies were also observed by Akhtar et al. (2009).

Particle size analyses were conducted for diatomite in the dust form. The distribution of particle size is shown in Fig. 6, while the particle size parameters are listed in Table 1. According to the study, the mechanical processing method used at the processing plant allows to obtain a fraction of diatomite, in which the majority are particles smaller than 10 μ m. Furthermore, the BET specific surface area of diatomite was

amounted to $12.22 \text{ m}^2 \text{ g}^{-1}$. Similar result was reported by other authors (Liguang and Hongyang, 2020) disc-shaper diatomite after treatment.

The results of the chemical composition analysis are presented in Table 2. The main component of the studied diatomite is amorphous SiO₂ in the amount of 68.52%. Additionally, it also contains Al₂O₃ in the amount of 11.78%. Al₂O₃ content is higher than standard. This is due to the presence of kaolinite in the diatomite (Saponjić et al., 2015). Moreover, the material contains a small amount of impurities, such as Fe₂O₃, TiO₂, CaO, MgO, MgO, Na₂O, K₂O, P₂O₅. Occurring impurities may mask some of the porosity, which in turn may affect the permeability of the product (Taoukil et al., 2021). As in the studies by Reka et al. (2021) among the trace elements, the main presence was found for Ba (122 ppm). In addition, a high content of V (112 ppm), Rb (108 ppm) and Zr (101 ppm) was also noted. The lowest share among the examined elements was read for As (9 ppm). The presented results are similar to those obtained by other authors (Wu et al., 2022). For example, Taoukil et al. (2021) obtained similar values, incl. SiO₂, Al₂O₃, Fe₂O₃, except for the lower percentages of CaO, MgO and Na₂O. This allows to state that the analyzed diatomite is a material that can be successfully used as a building material. Loss of ignition was 9.97%. Also some authors (Pookmanee et al., 2011) have shown in their work that natural diatomite from China has a similar value of 9.3%.

Patterns of X-ray diffraction of raw diatomite and calcined diatomite



Granulation of the sorbent

Fig. 10. The oil absorbency of various forms of the diatomite.



Granulation of the sorbent

Fig. 11. The absorbency of diatomite in the delivery condition and after treatment with aggressive agents, depending on the granulation of the sorbent.

are presented in Fig. 7. The most characteristic peak at $2\theta = 26^{\circ}2\theta$ occurs in both diffractograms and it can be attributed to the silicon oxide phase (ref. code: 01-079-6238). Furthermore, the presence of aluminum oxide (ref. code: 04-004-5291), kaolinite (ref. code: 01-075-1593) and albite (ref. code: 00-009-0466) was also noticed. A comparison of the results of the qualitative analysis performed for diatomite before and after the calcination process showed that the mineral composition of both materials is the same. Moreover, the results of the quantitative analysis are listed in Table 3. According to the results, it can be concluded that after treatment, the albite content increases with decreasing kaolinite content. Albite is a mineral belong to the plagio-clase group, which is thermally stable up to 1000 °C (Alraddadi, 2020; Perumal et al., 2019).

Fig. 8 presents nitrogen adsorption-desorption isotherms of crude diatomite and calcined diatomite at 750 °C. According to the IUPAC classification, the resulting N_2 sorption isotherms can be described as type IV isotherms. This is due to the occurrence of pore condensation and indicates that the material is mesoporous (Chen et al., 2020, 2020ach et al., 2022; Luo et al., 2018). The shape of adsorption isotherms depends on the intensity of the adsorbate-adsorbent interaction, as well as on the pore size (Marczyk et al., 2021). For the obtained isotherms, a hysteresis loop of H3 type is visible, typical for slotted interparticle pores (Chen et al., 2020; Luo et al., 2018; Marczyk et al., 2021).

Specific surface area, pore volume and pore size results for the diatomite are shown in Table 4. It was observed that the specific surface area of the diatomite decreased by about 52% after calcination. Also, other authors (Ersoy et al., 2022) proved in their study that calcination contributed to a decrease in the specific surface area of diatomite. The authors suggested that the reduction in surface area may be caused by aggregation, which causes grain coagulation and compaction (Bailliez and Nzihou, 2004). In addition to the decrease in the specific surface of the diatomite, after calcination there was also a decrease in pore volume and an increase in pore size. Similar dependencies were obtained by other authors (Song et al., 2011) with increasing sintering temperature of diatomite. Tests carried out on a mercury porosimeter showed that the raw diatomite has a total porosity of about 32.4%. The use of an appropriate calcination process allows to increase this porosity to the level of 53.5%. The research conducted for granulated diatomite has shown that granulation without the use of a binder guarantees the maintenance of this porosity at the level of 52-55% (different variants of granulation). Other researchers (Ibrahim and Selim, 2010) in their work showed that calcination at 900 °C for 3 h contributed to obtaining a clear porous structure of diatomite. Calcination removed most of the impurities blocking the pores of the material. Kokunešoski et al. (2016) for diatomaceous earth achieved a relatively high porosity of about 65%, using pressing at a pressure of 40 MPa and sintering at a temperature of 1000 °C. The same authors in another work (Šaponjić et al., 2015) also noticed that increasing the sintering temperature above 1000 °C reduces the open porosity. By increasing the temperature to 1300 °C, at the pressure of 40 MPa, a decrease of the porosity to 52% was observed (Kokunešoski et al., 2016, 2016aponjić et al., 2015).

Material's reaction to heating is important in determining its technological properties (Reka et al., 2021). The choice of calcination temperature was optimized for the sorption parameters of the petroleum substances. Fig. 9 shows a diagram of the thermal analysis illustrating the changes in the material (heating effects). The thermogravimetric curve is the change in mass loss, and the differential thermal analysis curve is the rate of mass loss as a function of time and temperature (Hebda et al., 2013; Kalak et al., 2019). Fig. 6 shows changes in the mass of a diatomite sample as a function of temperature and time. Highest weight loss (8.54%), was observed in the first stage, up to 100 min of measurement. This corresponds to the recorded DTA curve and the designated exothermic peak extreme at about 604 °C. The total mass loss was 9.06%. The mass loss to the temperature of about 200 °C may result from the elimination of absorbed water in the material (Lach et al., 2016). Subsequently, the mass loss to a temperature of about 600 °C may be related to the combustion of organic matter occurring in diatomaceous earth and the dehydration of chemically bound water in the opal structure (Mohamedbakr and Burkitbaev, 2009). In the temperature range from 600 °C to about 1000 °C, the mass loss may be related to dehydroxylation of clay components (Reka et al., 2021; Tironi et al., 2012). Based on the measurements of thermal analysis, the temperature of 850-860 °C for 0.5-1h was selected as optimal for the calcination process of diatomite with granulation below 0.063 mm.

Table 5 details the natural radioactivity concentrations of ⁴ K, ²²⁶Ra, and ²³²Th in the analyzed diatomite. Based on the measured activity concentrations of radionuclides the f₁ and f₂ factors were calculated. The highest f₁ indicator obtained for diatomite amounted to 0.59 ± 0.05 , whereas f₂ stood at 67.77 \pm 8.87 Bq kg⁻¹. The values of the activity indicators determine the possibility of approving raw materials and building materials for specific applications (Lewicka et al., 2022). According to the Polish law materials with activity indicators amounting to 1 and 200 Bq kg⁻¹ for f₁ and f₂ factors, respectively, may be used in buildings destined for human and livestock occupancy (Śleziak and Duliński, 2019). As a result of the study, it was found that all examined diatomite (different variants) from Jawornik Ruski comply with the requirements described in the Regulation of the Council of Ministers of December 17, 2020.

Fig. 10 shows the results of oil absorption tests for different diatomite

variants. Due to its use as a sorbent used on roads (collision sites) and in other facilities where there is leakage of petroleum substances, an aggregate or granular form is required (with the amount of dust up to 10–15%). As a result of calcination and screening, it was possible to obtain a sorbent with an absorption capacity of 96%. The addition of calcined diatomite dust, in accordance with the applicable regulations, increases this absorption to the level of 107%. In order to obtain the level of 130% for the sorbent in a compact form, a multivariate granulation study was carried out. The obtained granules reached the absorbency level of 124% (for the 0.4–0.9 mm fraction). The addition of calcined diatomite dust increases this level to (over) 130%. The conducted studies of the absorption of petroleum substances confirmed the achievement of the absorption level of 164% for the diatomite in the form of a powder.

Furthermore, in the next step the absorbency of the diatomite was tested (Fig. 11), depending on the applied treatment with aggressive agents, such as 5M solution sodium hydroxide (5M NaOH), hydrochloric acid (HCl), 3% solution of hydrochloric acid (3% HCl), sulfuric acid (VI) (H₂SO₄), and 3% solution of sulfuric acid (VI) (3% H₂SO₄). Moreover, raw diatomite without chemical treatment was used as reference material. Regarding the impact of the highly concentrated solution, such as HCl and H₂SO₄ on the diatomite, the presented results show the absorbency was higher in the case of raw material than after this chemical treatment. Moreover, taking into account the granularity of the sorbent, it should be noted that using solutions such as 5M NaOH, 3% HCl and 3%H₂SO₄ in the diatomite treatment process, generates much higher absorption in the case of diatomite with a particle size in the range of 0.5-3 mm, than its counterpart with larger particles (2-5 mm). The highest absorption capacity of oil was obtained by diatomite with a particle size of 0.5-3 mm after treatment with 5M NaOH.

5. Conclusions

The purpose of this study was to present the characteristics of Polish diatomite and the possibilities of its application. According to the results obtained, the diatomite from Jawornik Ruski in Poland is a suitable raw material for the absorption of petroleum substances. Thermomechanical processing of diatomite is an important part of material preparation, determining the mineralogical composition, specific surface area, as well as particle morphology.

Diatomite presented in this article is a material with high development potential, due to its ability to achieve high absorption of petroleum substances, even surpassing commercially available products.

As a result of the conducted research, it was found that.

- 1. Diatomite of Polish origin is a safe material and can be used as a sorbent for petroleum substances
- 2. The thermal treatment of diatomite allowed to obtain a product characterized by the sorption of petroleum substances at the level of over 100% by weight. This corresponds to the best parameters currently offered on the market or even exceeds these parameters.
- 3. The development of a domestic product in Poland, capable of absorbing large amounts of petroleum substances, may contribute to the increase in the availability of this material and increase its use, which will result in less oil spills being released into the natural environment.

The conducted research allows expanding the possibility of commercial use of locally occurring diatomite mainly as a sorbent for petroleum substances. So far, the sorption levels obtained by the mine owner were around 65–70% and the product was not marketcompetitive. Through advanced research and precise thermal analysis, it was possible to select the parameters of the calcination process and it is now possible to produce a diatomite sorbent with sorption levels for petroleum substances in the range of 100–130% by weight. This is of great importance from the point of view of the availability of such materials, as well as financial and environmental significance. The introduction of the product to the market will contribute to lowering the price of sorbents, as well as to their more efficient use. The conducted studies of the properties of diatomite also allow the transfer/implementation of these results to other applications, e.g. in agriculture or additives for plastics or concrete, which is currently being studied and will be presented in thematically separate scientific articles.

The diatomites described in this article are not typical diatomites containing large amounts of diatoms. Also, the SIO_2 content is lower than in competing diatomites available on the market. However, despite this, it appears that careful analysis of the physico-chemical properties, as well as thermal analysis, makes it possible to select appropriate thermal treatment conditions for the diatomite in order to achieve sorption levels superior to competing diatomites, which have a more conventional chemical and phase composition for this type of mineral. This achievement suggests that we can also obtain top-performing products from many other mining raw materials. This is particularly important in these times of energy and raw material crisis. Anything that can be done to save energy, fuel or raw materials will have a financial impact at a later date.

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CRediT authorship contribution statement

Michał Łach: Conceptualization, Formal analysis, Resources, Supervision, All authors have read and agreed to the published version of the manuscript. Kinga Pławecka: Methodology, Investigation, Writing - original draft, All authors have read and agreed to the published version of the manuscript. Joanna Marczyk: Methodology, Investigation, Writing - original draft, All authors have read and agreed to the published version of the manuscript. Celina Ziejewska: Methodology, Investigation, Writing - original draft, All authors have read and agreed to the published version of the manuscript. Maria Hebdowska-Krupa: Methodology, Investigation. Marek Nykiel: Formal analysis, Writing review & editing, All authors have read and agreed to the published version of the manuscript. Marek Hebda: Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing, Supervision, All authors have read and agreed to the published version of the manuscript. Krzysztof Miernik: Formal analysis, Writing - review & editing, Supervision, All authors have read and agreed to the published version of the manuscript. Dariusz Mierzwiński: Methodology, Investigation, Writing - review & editing, All authors have read and agreed to the published version of the manuscript. Kinga Korniejenko: Conceptualization, Writing - original draft, All authors have read and agreed to the published version of the manuscript. Janusz Mikuła: Resources, Writing - review & editing. Krzysztof Smoroń: Formal analysis, Writing - review & editing, All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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