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THE USE OF DIATOMACEOUS ROCKS OF GREEK ORIGIN AS ABSORBENTS OF OLIVE-OIL WASTERS

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Abstract

Diatomite is a multifunctional industrial mineral, having commercial interest in the food/agricultural and the construction sectors and also in environmental applications. Certain diatomite deposits worldwide are used as absorbents and filtering media in industrial scale. In Greece, several types of diatomaceous deposits (calcareous, clayey or amorphous phases-rich) occur in marine or lacustrine Tertiary basins. Bulk samples originated from western Macedonia, Thessaly and the islands of Samos and Milos were characterized, tested and compared concerning their absorption ability against olive mill wastes. The results of the current research show insignificant variations in the absorption ability of the tested Greek diatomites exhibiting equal or better behavior than some of the commercially used absorbents, either diatomaceous, or clayey. Hence, the Greek raw materials could find applications in the prevention of seashores and river banks pollution from the acidic olive-oil wastes.

Key words: *diatoms, olive-oil wastes, opaline silica, absorption, clay minerals.*

1. Introduction

Biogenic amorphous silica (opal-A) sedimentary deposits characterized as diatomaceous rocks or diatomaceous earth are represented by accumulations of diatom frustules, sponge spicules, radiolarian cells and/or silicoflagellate skeletons. Besides opal-A, diatomaceous rocks may contain carbonate and clay minerals, quartz, feldspars, micas and volcanic glass.

The physical and chemical properties which make diatomite a multifunctional industrial mineral include its low density, high porosity, high specific surface area, abrasiveness, insulating properties, inertness, absorptive capacity, brightness, and high silica content.

Almost all types of the diatomites have found industrial applications, utilized as chemicals, filter aids, fillers, absorbents, construction materials, environmental protection, civil engineering, agriculture, paint additives and catalysts.

Current world statistics show that the absorption applications of diatomite are about 13% of their total consumption (Crosley, 2002; Leahy, 2006). The last 50 years, clayey diatomite or diatomite-bentonite/zeolite mixtures are used to absorb industrial liquid spills. The material is used as granules and/or powders of various grades. Sometimes the natural samples are calcined to increase the hardness of the grains, to improve durability after absorbing a fluid, and to eliminate dust production.

In Greece, even though several diatomite deposits have been identified in the mainland and several islands of the Aegean and Ionian seas, only one deposit located in SW Milos Island is accidentally used as pozzolana, along with the interbedded tuffs (Fragoulis *et al.,* 2002).

During the production of olive oil, a large volume of waste water is generated and subsequently discarded. It is estimated that in the Mediterranean Basin alone, OOW accounts 10-12×106 m^3 each year (Cabrera *et al.,* 1996). OOW is considered one of the "heaviest" biomechanical byproducts mostly due to its organic load, with Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) that can reach up to 100 and 220 g/L, respectively (Stamatakis *et al.,* 2009).

Many different methods for the degradation of the wastes have been proposed, the majority of them involving physicochemical and microbial treatment of the wastes (Niaounakis and Halvadakis, 2006; McNamara *et al.,* 2008).

Diatomite and bentonitic clays have been successfully used as absorbent of olive oil wastes (OOW) (Al-Malah *et al.,* 2000; Makri and Stamatakis, 2005; Stamatakis *et al.,* 2009). More specifically, Greek origin calcareous diatomite retains about 86% of the phenolic compounds present in the OOW, whereas its ability to absorb the total dissolved salts is 82% and of the residual solid up to 74% (Makri and Stamatakis, 2005). Diatomites also increase the originally acidic pH of these wastes.

In general, the composition of the OOW varies according to the olive tree species, the harvesting period, the maturity of the olives, the climatic conditions in the specific area, the machinery and the technology of each olive processing plant is equipped (Borja-Padilla *et al.,* 1990; Fiestas Ros de Ursinos and Borja-Padilla, 1992).

According to literature data, the organic compounds may reach up to 18%, followed by inorganic substances, mainly phosphates and potassium salts 2%, whereas 60% of the solids are sugars mainly fructose and mannose (Niaounakis and Halvadakis, 2006).

The aim of the present paper is to characterize and test the OOW absorption capacity of diatomaceous rocks originated from four Greek deposits, namely Kleidi-Florina [western Macedonia], Sarantaporo-Elassona [Thessaly], Chora, Samos Island and Xylokeratia, Milos Island [Aegean Sea]. In addition, a commercial pure diatomite sample was also tested and compared to the aforementioned samples. The sample was collected from a processing plant of filter-aid diatomite, based at Albacete, Andalusia Spain. The samples were also compared to literature data, in order to point out the sufficiency significance of the Greek diatomaceous deposits in industrial applications as absorbents.

2. Materials and Methods

2.1 Geological data

2.1.1 Kleidi, Florina lignite basin, western Macedonia

In western Macedonia, the Komnina, Vegora and Klidi-Florina basins host commercial grade lignite deposits of Upper Miocene age. Vegora deposit was mined in the past, whereas the Kleidi deposit is currently mined, eventhough there are a series of technical problems. The Komnina deposit is not exploited so far. In all three deposits clayey diatomite is developed as overburden. As a result, in both areas Vegora and Kleidi significant quantities of mining wastes are exposed, which have specific mineralogy and technical characteristics (Owen *et al.,* 2010).

The Kleidi area is part of a broader chain of Neogene basins in western Macedonia. The basin extends from southern Serbia, in a NNW-SSE direction, up to the hills of Kozani through the cities of Florina, Amynteo and Ptolemais. The specific chain of basins is almost 100 km long and 15 - 20 km wide (Ilia *et al.,* 2009).

Fe and Fe-Ca phosphates such as viviantite and anapaite occur, locally in abundance, in the quarry faces as replacements of plant debris and leaves, and spherical faecal pellets <1cm in size respectively.

2.1.2 Sarantaporo-Elasson Basin, Thessaly

Upper Miocene clayey diatomite rocks with thickness of more than 100m occur near Giannota and Lykoudi villages, north of Elassona town in Thessaly (Stamatakis and Koukouzas, 2001; Stamatakis, 2004). Bulk samples extracted from certain places of the basin have been tested for their suitability as a pozzolanic additive and the production of lightweight aggregates (LWA) (Fragoulis *et al.,* 2004).

The basin is part of the SE extension of the western Macedonian basins of Upper Miocene age and is associated with the Drymos-Elassona Basin that lies southern and contains also clayey diatomaceous rocks (Ilia *et al.,* 2009).

Fe-Ca phosphates such as anapaite and mitridatite (surface samples) and Fe-phosphates such as vivianite (borehole samples) occur in both basins in the form of organic material replacements (Stamatakis and Koukouzas, 2001).

2.1.3 Samos Island, east Aegean Sea

Diatomaceous rocks (opal-A-rich) are present in the uppermost beds of the Late Miocene sedimentary rocks of Mytilinii Basin, east Samos (Stamatakis *et al.,* 1989). At lower stratigraphic levels diatomite has been transformed to porcelanite (opal-CT-rich) as a result of the action of diagenetic alterations in a saline-alkaline environment. Most of the deposits are CaO-rich with medium silica polymorphs content (25-40%) such as those of Chora, Mavratzei and Kokkari stratigraphic sections (Stamatakis *et al.,* 1989). Some of the Samos deposits were evaluated as cement additives and for the production of synthetic wollastonite ($CaSiO_3$), because of their mineralogical and chemical composition and sufficient reserves (Bedelean *et al.,* 1998; Stamatakis *et al.,* 2000)

The opal-A and opal-CT-rich beds overlie a porcelaneous limestone that is rich in opal-CT (Stamatakis, 1988). Greenish tuff up to 20m thick partially covers the opaline rocks (Stamatakis *et al.*, 1989).

2.1.4 Milos Island central Aegean Sea

Milos Island is located in the Central Aegean Sea, representing an active member of the South Aegean Volcanic Arc. The substrate of the island is mainly composed of lavas and volcaniclastic rocks. Diatomaceous rocks of Upper Pliocene through Lower Pleistocene age, ranging in thickness from few centimeter up to ~20 meters have been located successively alternated and interbedded with ash, pumice and lapilli tuffs in various parts of Milos, such as in Xylokeratia and Frago in the SW coast, in Adamas Bay and in Alimia-Sarakiniko-Agia Irini located at the north coast of Milos. Some of the deposits have been tested as pozzolanic additive, due to their dual yielding of reactive silica phases, namely opal-A and volcanic glass (Fragoulis *et al.,* 2002; Stamatakis *et al.,* 2003)

In the active quarry of pozzolanic rocks, where dark-colored marlstone and lapilli tuffs are co-extracted with light grey pumice tuffs and yellowish-white diatomaceous rocks, two distinct snow-white

Fig. 1: The sampling sites (red diamonds)

diatomite beds with total thickness of 5m are developed. A black lava sill laterally penetrates the diatomite beds altering the amorphous opal-A to poorly crystallised opal-CT (Stamatakis *et al*. 2009).

2.2 Samples

2.2.1 Diatomaceous Rocks

Four bulk diatomaceous rock samples of 70 kg each were collected from Kleidi-Florina, Sarantaporo-Elassona, Chora-Samos and Xylokeratia-Milos. The Kleidi-Florina sample was extracted from the currently exposed 30m thick overburden of the lignite deposit, located north of Kleidi village, the Sarantaporo-Elassona sample was collected from currently developed trenches of 5m thick and 50m long, about 1km west of Lykoudi village, the Samos sample was collected from a technical outcrop up to 100m thick, ~ 1km north of Chora village, whereas the Milos sample is the thinnest among the others, having a total thickness of ~3m and was extracted from the interbedded tuffs in the TITANs Xylokeratia Quarry of Pozzolanas located in the SW part of the island, (Fig. 1). The Spanish sample is a very fine-grained snow-white industrial product that is widely used as filter-aid for filtering of beer and oils.

2.2.2 Olive oil wastes (alpechin)

The OOW used in this experiment was collected from a three-phase centrifugal olive processing plant (olive mill), located at Kyparissia, Messenia Prefecture, Greece.

All samples were fine-grained and homogenous. Their colour varied according to their mineral content; the Samos and Milos samples being poor in common clays have off-white colour, whereas the Kleidi and Sarantaporo samples are dark coloured due to their high clay minerals content.

2.3 Analytical Techniques

2.3.1 X-Ray Diffraction (XRD)

The mineralogy of two sieved fractions [<0.3mm and 0.3 to 1.7mm) of the crushed, milled [1min] and homogenized diatomaceous rocks was studied by X-ray diffraction, on a Siemens Model 5005 X-ray diffractometer in combination with the DIFFRACplus software package. The diffractometer was operated using CuKa radiation at 40 kV and 40 mA and employing the following scanning parameters: 0.020°/s step size. The raw files were evaluated by use of the EVA 10.0 program of the Siemens DIFFRACplus-D5005 software package.

2.3.2 Scanning Electron Microscopy (SEM)

SEM techniques were performed on a SEM-EDS JEOL-JSM5600. The SEM was performed on diatomite rock chips on a JEOL JSM-5600 microscope with an OXFORD LINK™ ISIS™ energy dispersive X-Ray Microanalyzer. Conditions: Acceleration Voltage 20 KV, Beam current 0.5 nA, Livetime 50 s, Beam diameter < 2 μm.

2.3.3 Chemical analysis and grain size

Chemical analysis by X-Ray fluorescence was performed on a XRF PHILIPS PW1010 XRF spectrometer and grain size measurements were performed by the SILAS granulometer at TITAN SA laboratories, based in Kamari Viotia Cement Plant.

2.3.4 Determination of oil absorption values

The absorption capacity of the samples was measured by a technique (oil absorption) followed by the British Geological Survey analytical laboratories at Keyworth (Inglethorpe 1992). Through a burette OOW is added drop wise to 1g of dry sample in a glass plate and mixed using a palette knife. The addition of oil ceases when a smooth paste is formed. The paste should spread without cracking or crumbling and should only adhere to glass plate. The aforementioned method was scaled up in order to simulate a semi-industrial trial trying the absorption capacity of up to 100g of dried raw material. The absorption experiments were conducted on the same day of the OOW sample collection.

3. Results

3.1 Mineralogy

All samples studied contain, besides the crystalline constituents, an amorphous silica phase (opal-A) as shown by the presence of a broad peak (hump) between 20^{o} and 26^{o} 2h in the X-ray diffractogram. Sieving of the samples in two fractions (<0.3mm and 0.3 to 1.7mm) resulted to samples with no mineralogical variation (Table 1). The main mineral phases of all diatomaceous rocks studied is the amorphous phase opal-A that is predominantly represented by diatom frustules of various sizes and degree of preservation and secondarily by silicoflagellate skeletons and sponge spicules (Fig. 2) (Stamatakis *et al.,* 2009).

The Kleidi-Florina deposit is characterized by its high non-expandable clay content and traces of dolomite. The Sarantaporo-Elassona deposit has the most peculiar mineralogy as it contains expandable clays such as smectite and vermiculite, and also micro-particles of biogenic opal-A.

The Chora-Samos deposit is characterized by its high calcite and aragonite content and the absence

Table 1. The main mineral phases in the diatomitic deposits.

Sample	Mineralogical Composition										
	O-A	Cc/Ar	VG	Ver	Chl	Qtz	Fld	Ill/Mc	Dol	Ka	Sm/Sap
SRD-1	MJ			MD	TR	MD	MD	MD			MD
SRD-2	MJ			MD	TR	MD	MD	MD			MD
KLF-1	MD				MD	MD	MD	MJ	TR	TR	
KLF-2	MD				MD	MD	MD	MJ	TR	TR	
SMS-1	MD	MJ				TR		TR			
SMS-2	MD	MJ				TR		TR			
MLS-1	MJ		TR			TR	MD	TR			MD
MLS-2	MJ		TR			TR	MD	TR			MD
SPN-1	MJ					TR					

O-A: opal-A, VG: volcanic glass, Cc: calcite, Dol: dolomite, Ar: aragonite, Qtz: quartz, Fld: feldspar, Chl: chlorite, Sap: saponite, Ill: illite, Mc: muscovite, Ka: kaolinite, Sm: smectite, Ver: vermiculite. MJ: major, MD: medium, TR: minor-trace component.
SMS: Samos, SRD: Sarantaporo-Elassona, KLF: Kleidi-Florina, MLS: Milos, SPN: Alba-cete, Spain. Opal-A and volcanic glass [amorphous phases] were distinguished by SEM analysis.

of clay minerals. Apart from traces of quartz, detrital minerals such as micas and feldspars are also absent. The Xylokeratia-SW Milos sample is characterized by its relatively high feldspar and saponite content and the presence of volcanic glass. All these minerals are most likely related to the weathering and alteration of volcanic derived parent rocks. The Spanish sample, being pure diatomite, is almost exclusively composed of opal-A.

Conclusively, Samos and Florina deposits are the poorest in opal-content, whereas the Spanish sample is the richest.

3.2 Texture of the amorphous phases

SEM analysis of several chip samples from each deposit revealed the differences in texture and degree of preservation of the diatom frustules and the other biogenic phases, a factor that might have a significant role in their absorption ability. The major differences are the following:

- Opal-A in Sarantaporo-Elassona deposit is almost exclusively composed of cylindrical diatom frustules, whereas few layers contain disk-shaped diatom species. The degree of preservation is high, as they retain their minute structure (Fig 2: A & B).
- The Kleidi-Florina deposit contains small amounts and sporadically disseminated disk-shaped diatom frustules in a clayey matrix. The degree of preservation is good to medium (Fig 2: C & D).
- The Xylokeratia-Milos deposit contains mostly broken diatom frustules and sponge spicules, most likely due to their detrital nature in a near shore environment (Fig 2: E & F).

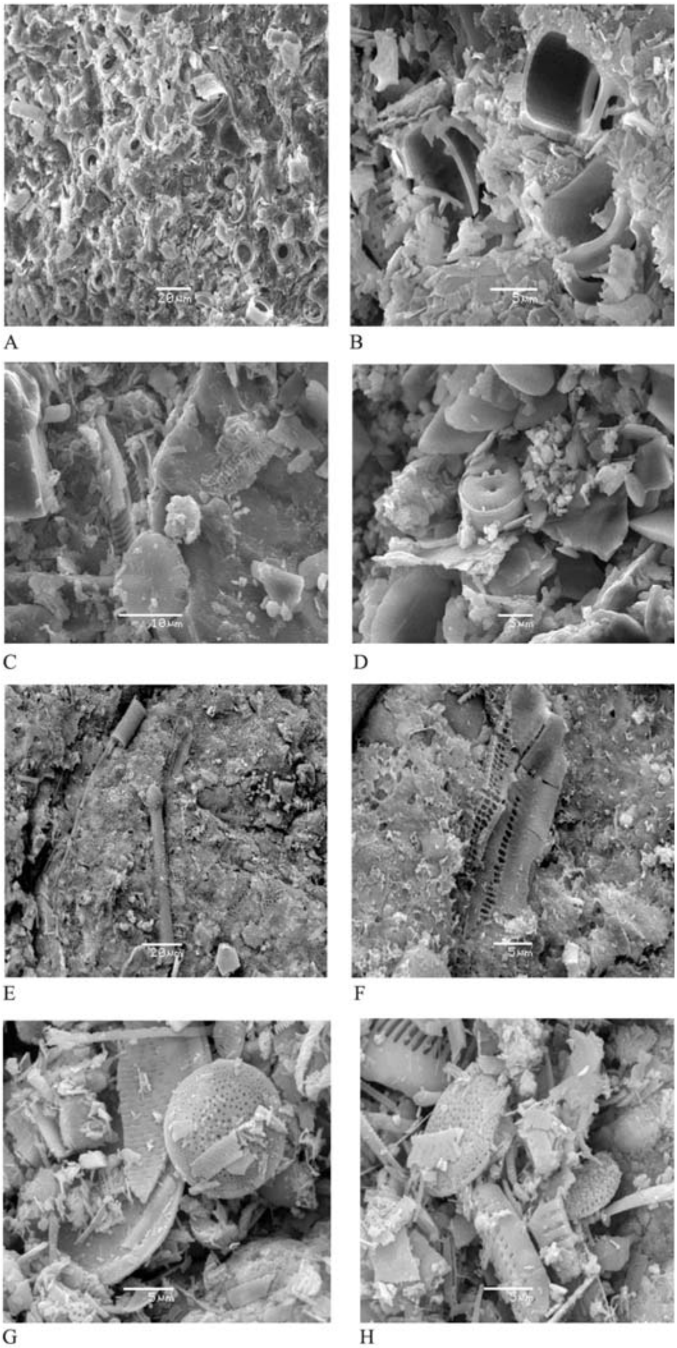


Fig. 2: SEM images of the samples studied. The Sarantaporo-Elassona sample is very rich in cylindrical diatom frustules [A, B]. Kleidi-Florina sample contains scattered diatom frustules in a clayey matrix [C, D]. Xylokeratia Milos sample contains reworked, broken diatom frustules and sponge spicules hosted in a glassy and clayey matrix [H, F]. Chora-Samos is composed of disk shaped and boat-like diatom frustules that exhibit medium degree of preservation [G, H].

Table 2. Major element chemistry of bulk samples of the diatomaceous rocks studied.

Sample	SRD	KLF	SMS	MLS	SPN
	Content%				
Na_2O	0.62	1.26	0.19	2.55	<0.1
K_2O	2.58	1.93	0.23	0.82	<0.1
CaO	1.82	3.34	29.60	2.72	0.82
MgO	0.95	1.86	1.09	1.11	0.12
Fe_2O_3	8.08	8.90	0.65	5.80	<0.1
Al_2O_3	17.83	15.40	4.36	6.42	0.15
SiO_2	61.11	63.60	36.84	70.83	95.85
LOI	7.37	3.78	26.62	9.50	3.20
Total	100.36	100.07	99.58	99.75	100.14

- The Chora-Samos deposit contains well preserved to intensely dissolved and broken disk-shaped and boat-like diatom frustules, due to diagenetic alterations at the lowermost part of the succession (Fig 2: G & H).

3.3 Chemical analysis

Major element analysis of the studied samples (Table 2) reflects their mineralogical composition. Hence, the carbonate minerals-rich sample of Samos has the highest CaO and LOI content. Alumina represents small amounts of clay minerals present. Silica is mostly applied to the opal-A silica polymorph. The high iron content of Sarantaporo-Elassona, Kleidi-Florina and Xylokeratia-Milos reflects their high amounts of clay minerals they contain. The higher MgO content of the Kleidi-Florina sample reflects its dolomite content. The highest alumina content of the Sarantaporo-Elassona and the Kleidi-Florina reflects their high content of aluminosilicate minerals (Tables 1 & 2). The chemically purest sample, concerning its total silica content is that of Albacete, Spain. The highest amount of potassium recorded in the Sarantaporo-Elassona sample is attributed to the presence of significant amounts of vermiculite and illite/muscovite.

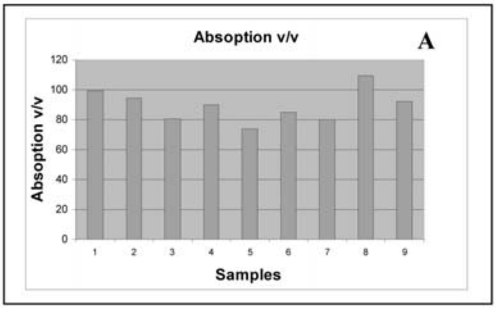
3.4 Absorption capacity

In general, in various applications diatomite is used in natural, calcined or flux-calcined form. For absorption applications, diatomite is used in natural form and also calcined at temperatures from 400 up to 850^oC (Georgiades and Stamatakis, 2010; Ilia *et al.,* 2009).

After their characterization, all samples were tested for their efficiency to absorb olive-oil wastes. Even though most of the currently used techniques grind the samples to obtain the <75μm fraction, we tested the industrially used size fraction of 0.3mm to 1.7mm, as well as the fine residual that has diameter <0.3mm. The samples absorption capacity was measured as described in Materials and Methods. The apparent density of the absorbent, as well as the specific gravity of the olive-oil wastes were measured and calculated respectively. The results are shown in Table 3.

Table 3. Technical characteristics of the samples studied and the olive-oil wastes.

	Sarantaporo		Spain	Milos		Samos		Kleidi	
Grain size [mm]	**<0.3**	**0.3-1.7**	**<0.3**	**<0.3**	**0.3-1.7**	**<0.3**	**0.3-1.7**	**<0.3**	**0.3-1.7**
Absorbent									
Mass [g]	27.5	34.0	4.6	25.7	28.4	29.1	34.5	40.2	36.0
Volume [mL]	49.5	51	31.0	50	50	50	52.5	53.5	46.0
Apparent Density [g/mL]	0.56	0.67	0.15	0.51	0.57	0.58	0.65	0.75	0.78
Olive oil wastes									
Volume [mL]	49.3	48.0	25.0	45.0	37.0	42.5	42.0	58.0	47.2
Mass [g]	50.2	48.9	25.5	45.8	37.7	43.3	42.7	58.7	48.9
Absorption %									
v/v	99.6	94.2	80.6	90.0	74.0	85.0	79.8	109.7	92.5
w/w	182.5	144.0	551	178.4	132.7	148.5	124.0	146.0	135.8



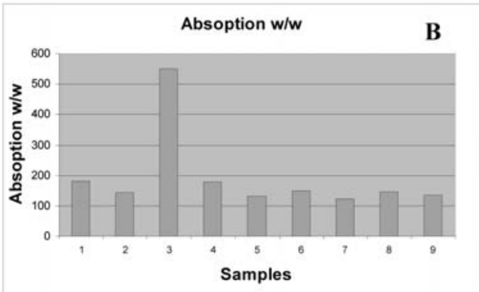


Fig. 3: Absorption capacity v/v% (A) and w/w% (B) of the studied samples [1 & 2 = Sarantaporo fine and coarse fraction, 3 =Spanish commercial sample [filter-aid], 4 & 5 = Milos fine and coarse fraction, 6 & 7 = Samos fine and coarse fraction, 8 & 9 = Kleidi fine & coarse fraction].

4. Discussion

As shown in Table 3 and Figure 3, the finest fraction of the samples [<0.3mm] has better absorption capacity than the 0.3-1.7mm fraction of all the Greek samples studied. This experimental observation can be attributed to the lower apparent density of the samples, and hence to their higher porosity. In Table 4 is pointed out the relation of the fineness of the particle sizes with the absorption capacity, whereas the amount of the wastes absorbed from each sample are presented in Figures 4 and 5, where it is clearly shown the association of the absorption capacity with the apparent density and the fineness of the sample. The higher absorption capacity of the finest fractions is due to both the finest particles of the clay minerals and the diatom frustules present in the samples. However, the highest absorption capacity of the Spanish sample is exclusively due to the diatom frustules absorption efficiency, as any clay or detrital minerals are practically absent.

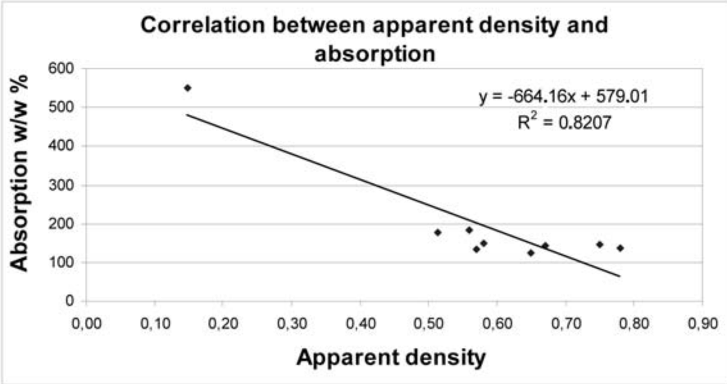


Fig. 4: Correlation between the apparent density and the absorption capacity of the samples studied.

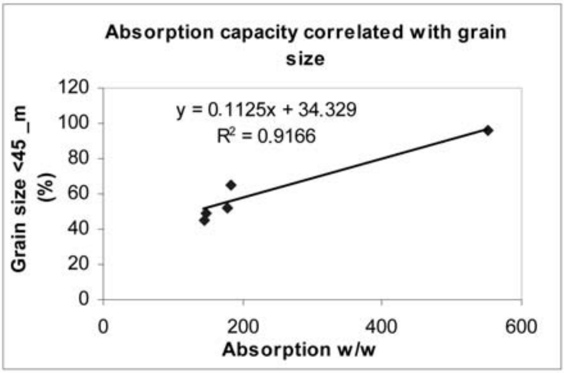


Fig. 5: The relation of the fineness at <45μm passing grain size and the absorption capacity [<0.3mm fraction].

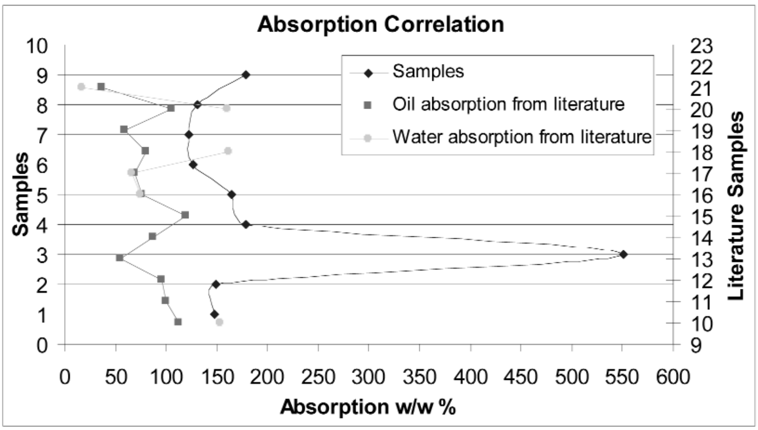


Fig. 6: Correlation of the Absorption Capacity of the nine samples measured [blue points] with literature data [red and yellow points] obtained from testing on oil and water absorption of commercial and laboratory samples of clayey and/or diatomaceous rocks (Makri and Stamatakis 2005; Georgiades and Stamatakis 2010; Ilia *et al*. 2009), Ediafilt kft – Hungary data sheet, 2009).

Table 4. Correlation of the fineness at <45μm passing grain size % and the absorption capacity [<0.3mm fraction]

absorption w/w	**182.5**	**551**	**178.4**	**148.5**	**146**
Grain size passing 45μm %	**65**	**95.6**	**52,3**	**49**	**45.5**

A correlation of the absorption capacity of the samples studied with literature data obtained from testing on oil and water absorption of commercial and laboratory samples of clayey and/or diatomaceous rocks is presented in Figure 6 (Makri and Stamatakis, 2005; Georgiades and Stamatakis, 2010; Ilia *et al.,* 2009).

In general, the samples studied as olive-oil waste absorbents exhibit equal or even better behaviour than the commercial or laboratory produced absorbents of reference oil and water, based on opal-A and/or clayey constituents. This is an indicator that the Greek diatomaceous rocks either clayey or calcareous might be tested in pilot-plant or an industrial scale to utilize them as industrial absorbents.

4. Conclusions

The olive-oil waste waters Absorption Capacity of the Greek studied diatomaceous rocks, ranges from 182.5% w/w to 124% w/w for Sarantaporo (<0.3mm) to Samos (0.3-1.7mm) samples respectively. The Spanish sample being a high added value specialty used commercially as filter-aid, has much higher absorption capacity. The higher absorption capacity of the Sarantaporo Elassona sample most likely is attributed to the predominance of expanded clay minerals that have high absorption capacity such as smectite and vermiculite, and cylindrical diatom frustules in that sample, whereas the other samples are richer in other clay minerals and/or detrital constituents and carbonates.

The given measurements indicate that all the examined diatomite bulk samples are appropriate for use as absorption materials in an industrial scale. Literature data classifies as efficient absorbents powder samples that have an efficiency to absorb up to 60-70% of their weight in liquid, hence the samples studied are appropriate for such applications (Crosley, 2002).

A realistic price for such an industrial absorbent might be ~100$/tn. Hence techno/economic assessment on certain diatomaceous deposits located close to olive-oil producing plants has to be carried out [i.e. in Samos, Lesvos, Zakynthos Crete and Milos islands, and also in Thessaly and in southernmost areas, where the major olive-oil industries and diatomaceous rocks have already been located. The used material could be used in local brick-making factories as source of silica, alumina and burnable matter. Trials on the efficiency of the diatomaceous rocks studied as absorbents of cheese waste-waters are currently being in progress.

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