Application of Natural and Synthetic Microporous Materials for Engine Oil Leakages Treatment: A Comparative Study

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We live in the era of growing industrialization and development of automotive industry. Those terms are undeniably related to an increasing demand for materials like crude oil and petroleum products. The everyday use, transportation and distribution of those substances unfortunately leads to an increase in the potential risks such as oil spills. Oil contamination is recognized as one of the major environmental issues nowadays with many consequences on the environmental and human health (Carmody et al., 2007). The removal of oil leakages can be made by oil absorption process techniques using various absorbents. Natural mineral sorbents offers satisfactory results because of the ease of their use, their stability, their need for specific surface area and their low cost. Their remarkable performance is based on their ability to absorb and immobilize the substances without releasing them under pressure (Franus et al., 2014). The microporous structure and the sorption property that zeolites exhibit, make them a promising material for the removal of petroleum substances.

Sorbents can be classified as hybrid systems, as they can be employed for active removal as well as for containment, and are particularly effective in recovering traces of oil from both land and water (Carmody et al., 2007). Also, sorbents are a class of materials which sorb oil either by absorption or adsorption. Past few decades have seen elaborate exploration of synthetic organic, inorganic, and natural organic sorbents, with a greater interest in the latter materials (Adebajo and Frost, 2003). Earlier observations (Franus et al., 2014) showed the potential use of synthetic zeolites as sorbents of petroleum substances as individual so as additives for enhancing the product. Also, the use of expanded perlite in combating oil spills have been examined (Roulia et al., 2002). Owing to their relative abundance, and due to the biodegradability of some of these, use of mineral sorbents has gained traction lately. However, no study has considered the comparison of natural and synthetic materials.

The goal of this study was to indicate the probability of microporous materials, examined globally, in order to compare and ensure the best possible solution with regard to the absorption of petroleum products. By comparing different grain sizes and most of all different materials we can have a comprehensive picture of their potential use. Both on the basis of the composition and on the basis of the structure of each material, behaves differently, as a result it has a different capacity in terms of absorption in general and in particular in petroleum products.

Three bulk samples of natural zeolites derived from different locations and one sample of synthetic zeolite derived from hydrothermal processing of fly ash (Koukouzas et al., 2009, 2010, Itskos et al., 2015) were used. Particularly, natural zeolite samples were derived from the Greek islands of Samos and Kimolos (Z-SAM and Z-KIM), and Pitigliano, Tuscany Italy (Z-IT), whereas the fly ash was derived from Meliti Power Plant Station (SYN-Z). For comparison of the absorption capacity of the samples, a calcareous diatomite bulk sample was used, originating from Mytilinii, Samos Island, Greece (DIAT).

For the study, five different grain fractions of each natural zeolite material (s1 > 1mm, 1mm< s2 >500μm, 500μm< s3 >250μm, 250μm< s4 >63μm and s5 <63μm) were used in order to determine the most suitable grain size for such application. With regard to the petroleum products, were used two types of oil: (1) High viscosity oil (SHELL HELIX HX5 20W-50) and (2) Low viscosity engine oil used in SEM Siemens-5000 instrument.

The mineral composition of the sorbents was investigated by X-ray diffraction. The particle size distribution and specific surface area was measured with a laser particle-size analyzer. The specific surface area refers to the total area of the unit mass of the material. It is an important indicator for evaluating the adsorption capacity. The experimental procedure was the standard test method for oil absorption by spatula. In particular, 3g of each solid absorbent material was placed on a 12x12 glazed surface and then the addition of the oil was made from the bottle drop by drop (using the glass tube) and after each addition was thoroughly mixed the oil and the sorbent by rubbing with the spatula. Continuing the addition of the oil till exactly enough oil has been incorporated to produce a very stiff paste that does not break or separate. The experiments were carried out in 3 repetitions.

Textural parameters such as BET surface area, pore volume, average pore width and the results of oils sorption of the investigated sorbents are summarized in the Table 1. The results of oil absorption capacity using the low viscosity oil were similar.

The results indicate that the sorption capacity of the investigated materials is controlled mainly by the textural parameters of the materials, especially specific surface area and diameters of pores. The studied zeolites differed in the contribution of micro- and mesopores in the surface and diameters of mesopores. In general, lower specific surface area and smaller grain fractions leads to lower oil absorption.

By comparing all the samples tested it's evident that the material with the best absorption capacity was the natural zeolite from the island of Kimolos and especially the grain fraction <63μm that was able to sorb 1.8ml/g of high viscosity oil. That high sorption capacity may be related to the larger surface area.

According to the literature data (e.g. Georgiadis & Stamatakis, 2009) all zeolite materials tested, could be assumed as functional in terms of their sorption capacity, with the finest grain fraction of Kimolos natural zeolite sample (Z-KIM s5) exhibiting the best performance.

Table 1. Textural parameters and absorption capacity for the high viscosity engine oil SHELL HELIX HX5 20W-50

Sample	Grain size	Absorption capacity (ml/g)	BET Surface Area (m^2/g)	Average pore width (Å)	Single point adsorption total pore volume (cm^3)
Z-KIM (s1)	>1mm	0.2			
Z-KIM (s2)	1mm – 500μm	1.0			
Z-KIM (s3)	500μm - 250μm	1.4			
Z-KIM (s4)	250μm - 63μm	1.5			
Z-KIM (s5)	<63μm	**1.8**	22.4	1365.9	0.8
Z-IT (s1)	>1mm	0.4			
Z-IT (s2)	1mm – 500μm	1.3			
Z-IT (s3)	500μm - 250μm	1.4			
Z-IT(s4)	250μm - 63μm	**1.7**	20.0	2368.6	1.2
Z-IT (s5)	<63μm	1.3			
Z-SAM (s1)	>1mm	0.3			
Z-SAM (s2)	1mm – 500μm	1.1			
Z-SAM (s3)	500μm - 250μm	1.2			
Z-SAM (s4)	250μm - 63μm	**1.4**	18.5	114.8	0.9
Z-SAM (s5)	<63μm	1.0			
SYN-Z		**1.4**	18.6	1412.3	0.9
DIAT		0.9			

It can be conclude that the narrow pores are less accessible for viscous substances and macromolecular substances such as oils. As far as the mineral composition is concerns, the result showed that oil absorption was highest by the natural clinoptilolite and motmorillonite mixture of the Kimolos sample). Diatomite was characterized by the lowest sorption capacity with respect to the tested substances. Notably, the analyses also indicate the potential use of synthetic zeolites from lignite fly ash for the removal of oil spills.

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