



Sepiolite as an effective natural porous adsorbent for surface oil-spill

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ABSTRACT

The adsorption of oil, spilled on a surface, by a variety of mineral sorbents was investigated. Edible oil adsorption was low (mg oil/m² clay) on montmorillonite, high on sepiolite and extremely high on talc, suggesting that the magnitude of adsorption correlates with clay hydrophobicity. Despite the high adsorption on talc the efficiency (g oil/g clay) of the clay to remove the oil was low, reaching 60% removal, while complete oil removal was achieved by sepiolite and only 45% by montmorillonite. XRD, SEM and FTIR measurements support the suggestion that high oil loadings on sepiolite indicated adsorption mainly on external surfaces as multilayers accompanied by desorption of water. The adsorption of hydraulic oil spilled on a road pavement by a variety of mineral sorbents was studied. As found in the case of the edible oils, the most efficient (g oil/g clay) sorbent was high quality sepiolite reaching complete adsorption while, oil removal by two organo-clays only reached 50%. On a lower quality sepiolite oil adsorption increased from 84% to 97% upon preheating the clay up to approximately 300 °C, explained in terms of water loss. However, adsorption on the clay treated at 400 °C decreased non-dramatically, strengthening our suggestion that the oil can penetrate into the sepiolite tunnels but most of the adsorption is on the external surfaces in multilayers. Oil adsorption by the high quality sepiolite was nearly complete even at an oil/sorbent ratio of 6 (w/w) indicating the potential of this sorbent for oil removal.

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1. Introduction

Oil can refer to many different materials, including edible oils on one hand and on the other hand crude oil, refined petroleum products (such as gasoline or diesel fuel) or by-products, oily refuse or oil mixed in waste. In the food industry oil–clay interactions have focused on oil bleaching i.e., mixing a clay adsorbent with edible oils to remove undesirable color bodies such as carotene, chlorophyll and other contaminants including trace metals, peroxides and phosphatides [1].

Oil–clay interactions have also attracted great interest from a wide range of environmental aspects. The environmental applications are quite the opposite from the food ones since they involve oil remediation by adsorbing the oil on the clay, and in most cases from an aquatic phase. The severe, wide spread and challenging problem of marine oil spills [2–5] has led to several studies focusing on removal of oil by adsorption from aquatic systems [6–8]. Hydrophobicity and oleophilicity of the sorbents are primary determinants of successful oil removal from an aquatic environment along with high uptake rate and capacity and biodegradability of the absorbents [9,10]. Oil–sorbent materials can be categorized into three major classes: organic synthetic products, organic vegetable products and inorganic mineral products [11–20].

Clay minerals are considered to be very efficient and cheap sorbents due to their chemical and mechanical stability, high surface area and structural properties [7,21,22]. The phyllosilicate clay mineral montmorillonite, commercially known as bentonite, is specifically widely used as a sorbent due to its layered stature and especially high surface area (~800 m²/g). Although, sepiolite has a lower surface area than montmorillonite (~300 m²/g) due to its high porosity it has a broad spectrum of applications ranging from cosmetics, paints, bleaching agent, filter aid to an industrial adsorbent [6,23–26]. Few studies have reported the adsorption of oil by sepiolite however, all of these reports examined oil removal from aquatic systems [6,7,19,27].

Land-based spills, and more specifically on roads, although usually smaller (in volume) than marine oil spills are more common. Even though, oil spills on land are very common extremely few studies examined the sorption of oil from a non-aqueous system [8,28]. These studies reported that the adsorption of diesel, hydraulic oil, and engine oil by organo-clays and cotton was higher than by sand.

In the current study we explored oil (edible and hydraulic oil) remediation from a simulated road spill by applying several mineral sorbents including five clay minerals and sand. The kinetics of oil adsorption and adsorption capacities (at equilibrium) of the minerals were measured and compared to those of classical organo-clays. To characterize the oil–clay interactions XRD, SEM and FTIR measurements were obtained. The effect of thermal treatment of

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sepiolite on its adsorption capacity was studied as well. The capacity of sepiolite to adsorb the hydraulic oil was by far the highest which was attributed to its physical and chemical structure.

2. Materials and methods

2.1. Materials

Hydraulic oil (10-W 40) was purchased from Paz Shemanim (Israel). Common olive and soya oil were bought in a supermarket. Wyoming Na-montmorillonite (SWy-2) was obtained from the Source Clays Repository of the Clay Mineral Society (Columbia, MO), and kaolinite Supreme Kaolinite from the English China Clay. Talc was commercial Johnson & Johnson baby powder (talc not starch). Pansil and Pangel C150 sepiolites were purchased from Tolsa (Spain). Pansil has a much smaller particle size distribution and a higher content of pure sepiolite and therefore was denoted sepiolite-pure, whereas Pangel C150 was simply denoted sepiolite. Surface areas of montmorillonite and of sepiolite are 760 and 258 m²/g, respectively, as reported by suppliers. The surface area of talc was measured (standard EGME) and found to be 17 m²/g. Quartz sand (grain size 0.8–1.5 mm) was purchased from Shoshani & Weinstein (Israel). Octadecyltrimethylammonium bromide (ODTMA) and phenyltrimethylammonium (PTMA) were supplied by Sigma–Aldrich (Steinheim, Germany).

2.2. Methods

2.2.1. Edible oil (olive and soya) adsorption

2.2.1.1. Preliminary sorbent screening. The initial experiment to select the most promising sorbents included introducing olive oil (0.075 g) on a cotton cloth, covering the stain with montmorillonite, sepiolite, kaolinite or talc (0.5 g) reaching 15% oil/sorbent w/w for an overnight. The sorbents were removed (after 24 h) by extensive shaking and oil removal was determined visually. Partial removal was obtained in the cases of kaolinite but complete removal (visually) was achieved when talc, montmorillonite or sepiolite were spread on the stain.

2.2.1.2. Edible oil adsorption on talc, montmorillonite and sepiolite. Edible oil adsorption on talc, montmorillonite and sepiolite with surface areas of 17, 760 and 258 m²/g, respectively, and CEC of ~0, 0.76 and 0.15 mmol/g, respectively. The adsorption (24 h) of olive and soya oils (0.175 g oil) by talc, montmorillonite and sepiolite (0.5 g) i.e., 35% w/w oil/sorbent, was quantified. The sorbents (including the adsorbed oil) were collected from the cloth and the percent of carbon in the samples was measured by CHNSO element analysis. The amount of oil adsorbed was calculated. The olive oil and soya oils are composed of 93% and 96% of carbon, respectively. The percent of carbon in the clay samples is negligible (0.2–0.4%).

2.2.2. Hydraulic oil adsorption

2.2.2.1. Adsorption kinetics of hydraulic oil on selected sorbents. The adsorption kinetics of hydraulic oil (0.5 g) spilled on a road pavement by 1 g of sepiolite, sepiolite-pure, talc, quartz sand, fine sand and organo-clays (ODTMA-montmorillonite (1.2 mmol/g clay) and PTMA-montmorillonite (0.5 mmol/g clay) was monitored. Preparation of the organo-clays is described in [29]. After 4, 12, 24 or 48 h the sorbents (including adsorbed oil) were collected from the road pavements and analyzed by CHNSO element analysis to calculate the amount of oil adsorbed (in the hydraulic oil there is 80.3% carbon). The kinetic results were fitted to pseudo-first and second orders (Ho Y.S. and Chiang C.C). The fits to the second order were significantly higher. The calculated amount of oil adsorbed at

equilibrium (q_e) and rate constant (k) employing the integrated rate law for pseudo-second reaction are presented in Table 2.

2.2.2.2. Equilibrium adsorption experiment of hydraulic oil on sepiolite-pure. The adsorption of hydraulic oil at increasing loadings (from 30% to 600% w/w oil/sorbent) spilled on a road pavement by sepiolite-pure was measured at equilibrium (24 h). The amount of oil adsorbed was determined as described in Section 2.2.2.1.

Another approach was taken to measure oil adsorption on sepiolite from excess oil. The clay was set in an empty tea bag, dipped into a cup of the hydraulic oil, left to equilibrate overnight when teabag was removed, let to drip (excess oil) and oil content on the clay was measured as described (Section 2.2.2.1). Adsorption of the oil on the tea bag was negligible.

2.2.2.3. Thermal treatment of sepiolite for improved adsorption. The adsorption of hydraulic oil (140% w/w oil/sorbent) spilled on a road pavement by sepiolite was measured. The sepiolite was treated for 24 h at different temperatures (60, 105, 200, 300 and 400 °C). The amount of oil adsorbed was determined as described (Section 2.2.2.1).

2.2.3. Characterization of oil–clay interactions

2.2.3.1. X-ray diffraction. The basal XRD spacing of montmorillonite and motmorillonit adsorbed with soya or olive oil were measured (0.7 g oil/g clay). The basal spacing was measured using an X-ray diffractometer (Philips PW1830/3710/3020) with Cu K α radiation, $\lambda = 1.542$

2.2.3.2. Fourier transform infrared. FTIR spectra were obtained for montmorillonite and sepiolite, adsorbed with the edible oils (70% w/w oil/clay) and sepiolite adsorbed with the hydraulic oil (30–200% w/w oil/clay). Infrared spectra were obtained by mixing the samples with KBr to form pellets, using an FTIR spectrometer (Nicolet Magna-IR-550, Madison, WI). The FTIR spectra were recorded at room temperature in the range of 600–4000 cm^{−1}.

2.2.3.3. Scanning electron microscopy (SEM). The morphology of sepiolite-pure and sepiolite samples, non-treated and with oil (250 w/w% oil/clay), was studied by SEM and element analysis. Samples were prepared on Akulon stubs using double-sided sticky tape. The microphotographs are recorded using scanning electron microscope JEOL model, JSM-5410 LV available at the microscopy lab at the faculty of agriculture, food and environmental quality Sciences, The Hebrew University. The images are taken with an accelerating voltage of 20 kV, at low vacuum mode (28 Pa) and backscattered electron detector (BEI).

3. Results and discussion

3.1. Edible oil adsorption on talc, montmorillonite and sepiolite

The adsorption of edible oils (olive and soya) by talc, montmorillonite and sepiolite was further explored. The oil weight was increased to 35% (oil/sorbent w/w) and the amount of oil adsorbed is reported in Table 1. No significant differences were obtained between the olive and soya oil adsorptions.

The adsorption (g oil/g sorbent) of the olive and soya oils was the highest by sepiolite reaching 100% removal. Talc demonstrated intermediate adsorption (~60%), whereas, the adsorption by montmorillonite was relatively low (~40–45%). Higher oil adsorption on sepiolite in comparison to its adsorption on montmorillonite was also obtained for oil adsorption from water [6]. However, the adsorption efficiency (~20% removal and 0.18 g oil/g sepiolite)

Table 1

Olive and soya oil adsorption by sepiolite, montmorillonite and talc. Oil/sorbent weight ratio was 35%. The maximum standard deviation ± 0.02 g/g.

Sorbent	Oil	Oil adsorbed		
		g/g clay	mg oil/m ²	%
Sepiolite	Olive	0.36	1.40	100
	Soya	0.37	1.43	100
Montmorillonite	Olive	0.16	0.21	46
	Soya	0.14	0.18	40
Talc	Olive	0.19	11.2	54
	Soya	0.23	13.5	66

Table 2

Calculated amount of oil adsorbed at equilibrium (q_e) and rate constant (k) employing the integrated rate law for pseudo-second reaction.

Sorbent	q_e (g/g)	k (g/g oil h)	R^2
Sepiolite-pure	0.58	1.10	0.996
Sepiolite	0.49	1.40	0.9966
Talc	0.30	1.84	0.9943
Sand	0.17	0.63	0.8314
PTMA-mont	0.30	1.84	0.9943
ODTMA-mont	0.37	1.08	0.9922

form water was substantially lower than its efficiency in a dry system as examined in the current study.

Furthermore, when discussing the oil adsorption (Table 1) in terms of coverage (mg oil/m² sorbent) the adsorption on talc is by far the highest, reaching one and two magnitudes higher than the adsorption by sepiolite and montmorillonite, respectively. Although, the oils can intercalate in montmorillonite as obtained by XRD measurements (Fig. 1) the adsorption per m² was very low.

The XRD patterns of montmorillonite and of the montmorillonite adsorbed with olive and soya oils are shown in Fig. 1. Montmorillonite gave the expected basal spacing of 1.25 nm (additional 0.1-nm spacing due to illite impurities). The basal spacing of montmorillonite at oil loadings of 0.14–0.16 g/g increased to 1.43 nm, which can be attributed to the penetration of one oil layer. An increase in the basal spacing to ~ 1.3 nm upon the adsorption of *n*-heptane (extracted from crude petroleum) has been reported (Cosultichi et al., 2004). Similar increases in the basal spacings to those obtained in the current study (indicating the intercalation in a single layer) were observed for several polycations [30–32].

Taking into account that the thickness of a single oil layer is approximately 0.2 nm (as obtained from the XRD measurements) and the clays' surface area (in the case of montmorillonite internal and external) the coverage of the clay by the olive oil was calculated for the three clays. Oil coverage on montmorillonite reached 1.12 m² oil/m² clay, whereas, the coverage on sepiolite and talc reached 6 and 62 m² oil/m² clay, respectively. The extremely high coverage obtained on talc and the high coverage obtained on sepiolite suggest that the oil adsorbs on external surfaces as multilayers. In the case of sepiolite we suggest that a substantial amount of the oil adsorbs on the external surface of the clay but oil penetration in the structural tunnels also contributes to the total adsorption (see Section 3.6).

We suggest that oil adsorption increases with a decrease in charged sites on the clay which are compensated by hydrated exchangeable cations. The relatively low oil adsorption by montmorillonite is due to the clay's hydrophilic characteristics attributed to its high CEC = 0.76 meq/g and to its swelling properties. Sepiolite, on the other hand, has a substantially lower CEC (0.15 meq/g) [33], no swelling properties and well characterized neutral sites [34]. Talc has nearly no residual surface charges and little hydration resulting in high adsorption per m². However,

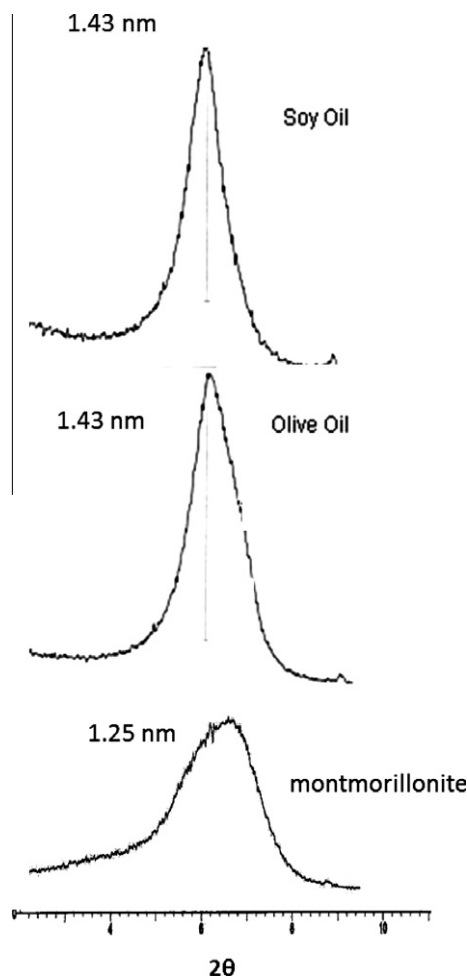


Fig. 1. XRD patterns of montmorillonite and of the montmorillonite adsorbed with olive and soya oils (0.7 g oil/g clay).

due to the low surface area of talc the adsorption per g clay is much higher on sepiolite.

The similarity between the structures of sepiolite and talc is well known. The sepiolite sheets formed by the apexes of the tetrahedrons are completed by hydroxyls and magnesium in octahedral coordination which tie the sheets together. A single ribbon is similar in structure to a layer of talc [35].

Finally, the removal of the edible oils was the most efficient by sepiolite (in terms of weight capacity g oil/g sorbent) and therefore, to further explore hydraulic oil removal we examined two grades of sepiolite; a high quality one denoted, sepiolite-pure and the lower quality sepiolite, applied in the experiments previously described and denoted, sepiolite.

3.2. Sepiolite characteristics

The morphology of sepiolite (Fig. 2B and E) and sepiolite-pure (Fig. 2A and D) samples was studied by SEM and element analysis. As seen in Fig. 2 the morphologies of the two samples are significantly different. In the sepiolite-pure microphotographs, the particles are much smaller, fibers can be clearly observed along with a few larger particles, the fibers are relatively small (a few μ m), look fluffy and the sample is relatively homogenous. In contrast, in the sepiolite microphotographs, very large aggregates are obtained (20–50 μ m) and the morphology of the particles resembles platelets rather than fibers. Similar results were reported for various grades of sepiolite samples [36].

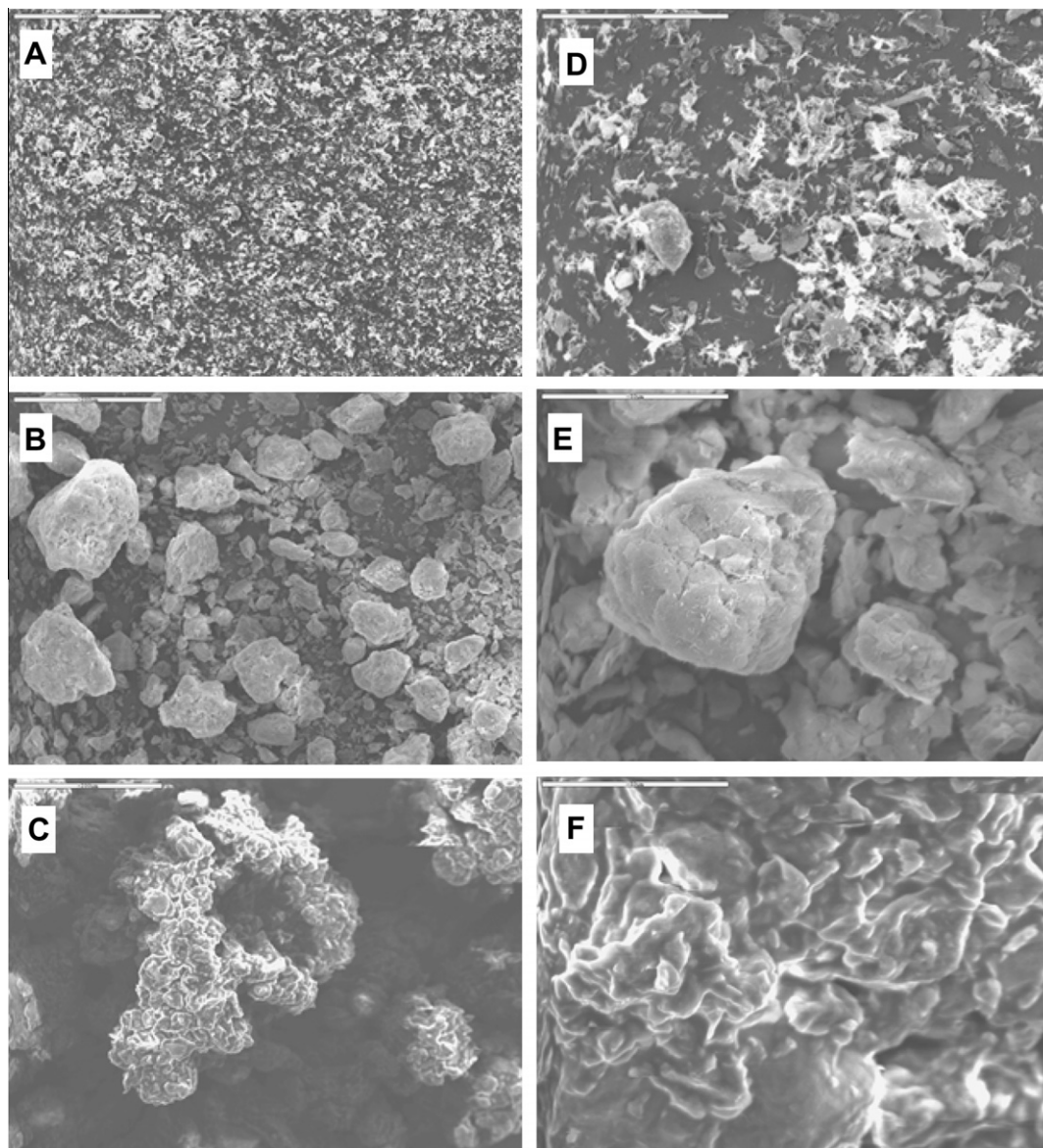


Fig. 2. (A) Sepiolite-pure, (B) sepiolite, (C) sepiolite adsorbed with 2.5 g oil/g (bar indicating 200 μm), (D) sepiolite-pure, (E) sepiolite and (F) sepiolite adsorbed with 2.5 g oil/g (bar indicating 50 μm).

3.3. Hydraulic oil adsorption

The adsorption kinetics of hydraulic oil (0.5 g) spilled on a road pavement by a variety of sorbents (1 g) was monitored (Fig. 3A). In all cases equilibrium was reached within 24 h (Fig. 3B). As obtained in the cases of the edible oils the most efficient (in terms of weight capacity g oil/g sorbent) sorbent for the hydraulic oil adsorption was sepiolite. At equilibrium complete oil removal was obtained by sepiolite-pure and nearly complete removal was obtained for the less pure sepiolite (~96%). Talc demonstrated intermediate efficiency (~45%) while sand and pure quartz showed low oil adsorption (30% and 8%, respectively).

The adsorption of the edible oils by montmorillonite in comparison with their adsorption by talc and sepiolite was low; therefore, the adsorption of the hydraulic oil was examined by organo-montmorillonite complexes which have been reported to improve oil adsorptions [8,28]. Indeed, the adsorption of the hydraulic oil by the tested organo-montmorillonites (ODTMA- and PTMA-mont) was as high as by talc but significantly lower than by sepiolite. The higher oil adsorption by ODTMA-mont in comparison with

its adsorption by PTMA-mont can be explained by solubilization of oil in the ODTMA micelles. Although, the employment of organo-montmorillonites may increase oil adsorption in comparison to its adsorption by untreated montmorillonite, the adsorption by untreated sepiolite is significantly superior and obviously cheaper.

The adsorption kinetics results were in good agreement with the integrated rate law for pseudo-second reaction (Table 2). The adsorption kinetics of the hydraulic oil on sand was significantly slower than by the secondary minerals and by the organo-clays. The differences in adsorption rate between the sepiolites and talc (and the organo-clays) are small. The slightly slower adsorption to the sepiolites may strengthen our hypothesis that a substantial amount of the adsorbed oil is on the external surface area and a small fraction adsorbs within the tunnels. Since substantial oil penetration in the sepiolite tunnels would most likely result in substantially slower kinetics [32].

The calculated amount of oil adsorbed at equilibrium (e_q) was significantly higher on the sepiolites with the highest adsorption on sepiolite-pure.

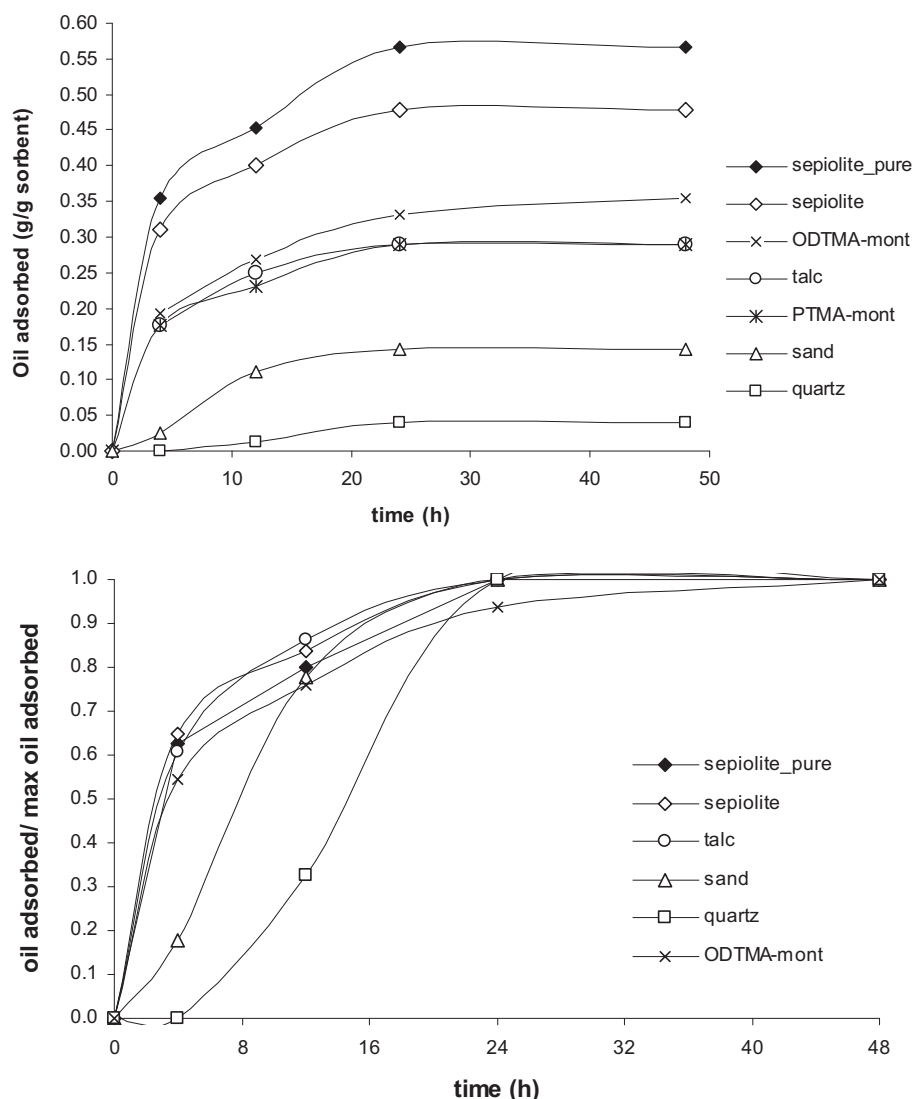


Fig. 3. Kinetics of hydraulic oil adsorption by sorbents (50% w/w oil/sorbent). The maximum standard deviation was ± 0.05 g/g.

3.4. Hydraulic oil–sepiolite interactions

3.4.1. Oil capacity on sepiolite

The capacity of the most promising sorbent, sepiolite-pure, was studied by increasing the oil weight (0.15–3 g) and covering it with the same amount of sorbent (0.5 g) (Fig. 5). Oil adsorption was nearly complete at all oil/sorbent ratios (0.3–6 w/w) i.e., the clay could hold oil six times its weight. Beyond this ratio it was hard to differentiate (visually while collecting the samples) between adsorbed and non adsorbed oil. Therefore, we concluded that the maximum capacity was 6 g oil/g sepiolite-pure. To further strengthen this conclusion we measured the adsorption of the oil by dipping the sepiolite in the oil (adsorption under saturation conditions). The clay was set in a tea bag, dipped into a cup of oil, left to equilibrate overnight when teabag was removed, let to drip (excess oil) and oil content on the clay was measured. The adsorption reached 5.8 g oil/g sepiolite-pure indicating that the capacity indeed is 6 ± 0.2 g/g as obtained from the initial experiment (Fig. 4).

3.4.2. SEM measurements

The changes in morphology of the sepiolite clay upon oil adsorption (2.5 g oil/g sepiolite) can be clearly seen in SEM images

(Fig. 2C and F). From a well defined aggregated structure and sharp edges of the minerals (Fig. 2B and E) the samples with the oil clearly look as if the oil gathered the particles together and that the edges are more round. Element analysis indicates that the dark areas in the samples with oil contain significant amounts carbon 40–60% (Fig. 2C and F).

3.4.3. FTIR measurements

The interactions between the hydraulic oil and sepiolite were further characterized by investigating the FTIR spectra (4000–550 cm^{-1}) of sepiolite adsorbed with increasing amounts of oil (0–2 g oil/g clay) (Fig. 5). The sepiolite spectra showed characteristic peaks at 3200–3660 cm^{-1} which correspond to the presence of different kinds of water (adsorbed, coordinated, and zeolitic) and to the presence of hydroxyl groups coordinated to metallic cations, especially Mg–OH bonds [33,36]. The band at 1640 cm^{-1} is attributed to the bending vibrational mode of coordinated water molecules. Additional characteristic bands of silicate structure can be seen at 1200, 1080, 1020 and 980 cm^{-1} . The peak at 1020 is attributed to the Si–O–Si plane vibrations, and the bands at 1212, 1080, and 980 cm^{-1} to Si–O bonds.

Upon the adsorption of the hydraulic oil additional bands attributed to the oil were observed at 1450, 2850, 2920 and

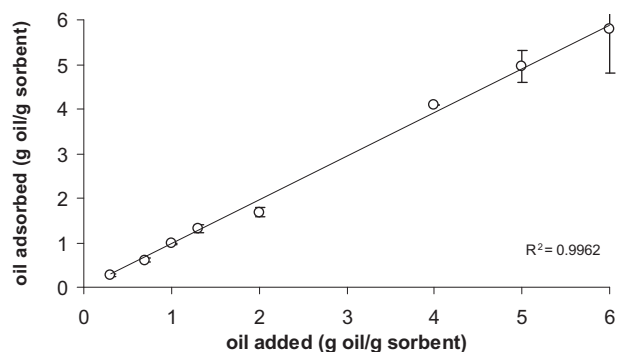


Fig. 4. Hydraulic oil adsorption by sepiolite-pure (30–600% oil/sorbent w/w%).

2940 cm^{-1} . The band at 1450 cm^{-1} represents CH_2 groups. The group of bands between 2850–3000 cm^{-1} corresponds to the C–H bands of alkane chains typical in oils. These bands have been reported for the adsorption on montmorillonite of alkane chains [37].

The main bands related to hydraulic oil 2850–3000 cm^{-1} and 1450 cm^{-1} increase linearly with the increase in oil adsorption up to 1 g/g and continue to increase not linear) at loadings up to 2 g/g. While the oil related vibrations increase the 3200–3660 cm^{-1} and the 1640 cm^{-1} vibration decrease supporting our suggestion that oil adsorption is accompanied by the desorption of water.

3.5. Thermal treatment of sepiolite for improved oil adsorption

Complete oil removal was achieved by the sepiolite-pure for a wide range of oil/clay ratios (Fig. 4), however, oil removal by the lower quality sepiolite was not complete at high oil loadings. For example, upon adding 140 oil/sepiolite w/w oil adsorption reached 84%. We hypothesized that the adsorption on sepiolite can be improved by pretreating the clay with heat due to desorption of the different waters from the clay structure at high temperatures. Indeed, oil adsorption increased from 84% to 97% upon an increase in the temperature applied for preheating the sepiolite and reached a maximum in adsorption at a pretreatment temperature of approximately 300 °C. Beyond this temperature a decrease in adsorption was obtained (Fig. 6). The adsorbed water in the channels is lost at about 100 °C, water in the channels attached to the

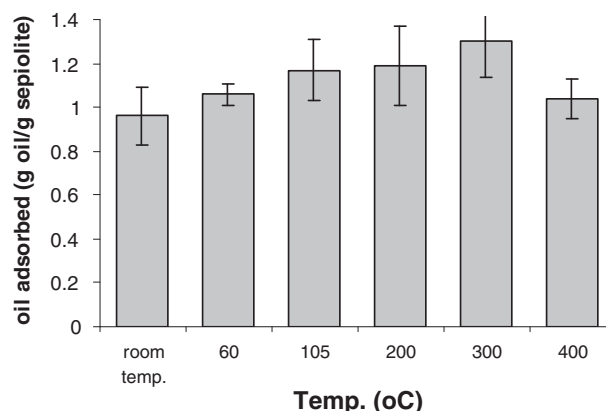


Fig. 6. Hydraulic oil adsorption by sepiolite (140% oil/sorbent w/w%) as a function of preheating temperature of the clay.

silicate units is lost between 275 and 375 °C, and hydrocyl water is lost from about 550 °C [38]. The increase in adsorption can be explained in terms of water loss from the clay structure which increases hydrophobicity and promotes oil adsorption. An increase in oil upon water loss is consistent with our suggestion that oil adsorption is higher on less hydrophilic clays such as talc and sepiolite.

There is no change in the structure of sepiolite upon heating to 350 °C. Above this temperature; the loss of water is accompanied by a change in the dimensions of the structure including tilting [35], which can explain the reduction in oil adsorption on the sepiolite treated at 400 °C. This decrease is not dramatic strengthening our suggestion that the oil can penetrate into the sepiolite tunnels but most of the adsorption is on the external surface of the clay in several layers.

4. Conclusions

The adsorption of oil (edible and hydraulic), spilled on a surface, by a variety of mineral sorbents was investigated. Oil adsorption was by far the most efficient (g oil/ sorbent) by high quality sepiolite. The magnitude of adsorption by the different sorbents (montmorillonite, talc, sepiolite, quartz and kaolinite) increased with the sorbents hydrophobicity. Oil adsorption by sepiolite was twofold

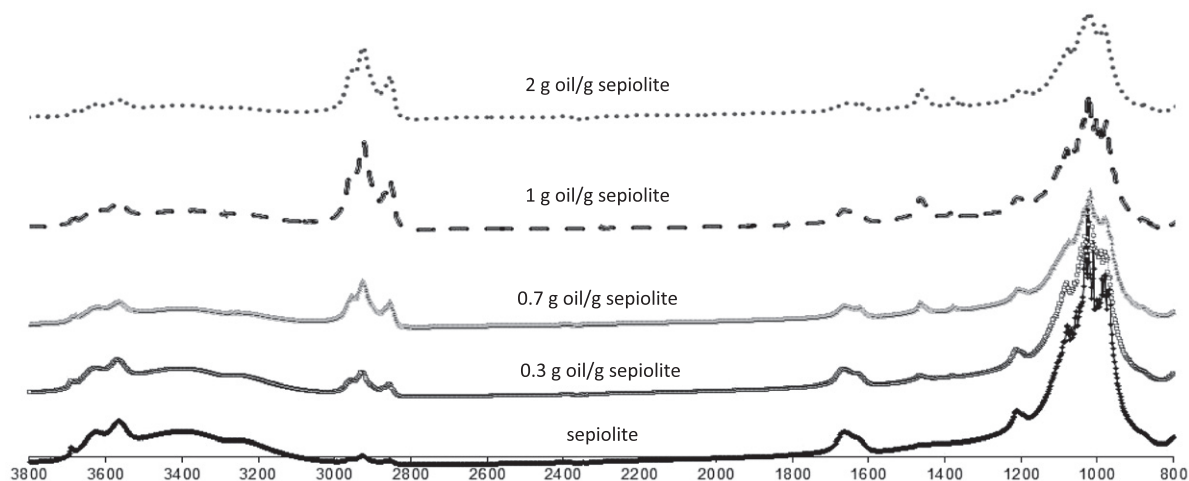


Fig. 5. FTIR spectra of sepiolite adsorbed with hydraulic oil (0–2 g/g).

higher than by organo-clays which have been recommended as good oil sorbents. XRD, SEM and FTIR measurements suggested that the oil adsorption on sepiolite is mainly on external surfaces as multilayers accompanied by desorption of water. Accordingly, oil adsorption on sepiolite pre-treated up to 300 °C increased. Furthermore, adsorption on sepiolite pre-treated at 400 °C decreased non-dramatically, indicating that the oil penetrates into the sepiolite tunnels but that most of the adsorption is external.

Land-based oil spills, and more specifically on roads, are more common than marine oil spills (although, usually smaller in volume) but their treatment is much less addressed. In this study we presented extremely high adsorption of hydraulic oil by sepiolite, 6 g/g, demonstrating the potential of sepiolite as a sorbent for surface oil spill treatment.

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