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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/m^2 clay) on motmorillonite, 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.

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 a long 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 m^2/g). Although, sepiolite has a lower surfaces area than montmorillonite (~300 m^2/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 form 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 simulate 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 m^2/g, respectively, as reported by suppliers. The surface area of talk was measured (standard EGME) and found to be 17 m^2/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 m^2/g, respectively, and CEC of $\sim$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 is 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, quart 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 Kα 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 adsorpiton 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 ($\sim$60%), whereas, the adsorption by montmorillonite was relatively low ($\sim$40–45%). Higher oil adsorption on sepiolite in comparison to its adsorption on montmorillonite was also obtained for oil adsorption from water [6]. However, the adsorption efficiency ($\sim$20% removal and 0.18 g oil/g sepiolite)