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Adsorption of crude oil on anhydrous and hydrophobized vermiculite

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Abstract

This publication reports the adsorption of crude oil on vermiculite samples, expanded and hydrophobized with carnauba (*Copernícia Cerífera*) wax. The adsorption studies were performed by using columns filled with the vermiculite matrices and by dispersion of the vermiculite samples in an oil–water (50 ppm of oil) emulsion. The hydrate vermiculite exhibits a very low adsorption capacity against crude oil. On the other hand, anhydrous (expanded) and hydrophobized matrices show a high adsorption capacity. The 10% hydrophobized matrix show a 50% increased adsorption capacity, in comparison with the expanded one. For adsorption performed in the water–oil emulsion, saturation of the solid hydrophobized matrix is achieved after 60 min. The hydrophobized samples exhibit adsorption factors in the 0.7–1.0 range.
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1. Introduction

Many inorganic compounds, such as molybdenum oxide, acid titanates, and titanium or zirconium phosphates, are lamellar; that is, they exhibit two inorganic layers separated by an interlayer distance *d* that interact with each other by van der Walls forces [1]. Such matrices can be employed for the synthesis of so-called intercalation compounds [2–4].

Taking into account their adsorption ability, clay minerals can be successfully hydrophobized with cationic surfactants [5]. Such hydrophobized matrices can be employed to promote the interlayer adsorption of many organic species, such as 1-pentanol [6].

Vermiculite is a mica-like lamellar mineral that rapidly expands upon heating to produce a lightweight material. This expanded (exfoliated) product is used as lightweight aggregate in concrete, plaster, and premixes. Horticultural and fertilizer products are also examples of compounds for which a large end use of vermiculite can be pointed out.

It has been verified that the hydration degree of the vermiculite clay matrix can exert remarkable effects on the magnetic properties of its intercalation compounds [7]. Furthermore, vermiculite has been recently employed in a series of studies involving the adsorption of oil-contaminated water samples [8,9].

The aim of this publication is to report the preparation and adsorption of crude oil on vermiculite samples hydrophobized with carnauba (*Copernícia Cerífera*) wax.

2. Experimental

The vermiculite samples used were supplied by the company União Brasileira de Mineração, from Santa Luzia, state of Paraíba, Brazil. For such vermiculite sample, the main components are (as oxide percentage): Si (44.7), Al (9.1), Fe (5.9), Mg (16.2), Na (0.6), Ca (5.1), K (2.7), and Ti (0.7); sulfur content: 0.2% (w/w); salt content: 862 mg NaCl dm^{-3}; paraffin: 13.6%.

The adsorption of crude oil was performed in dehydrated (expanded) and hydrophobized vermiculite samples, named here as EV (expanded vermiculite) and HV (hydrophobized vermiculite), respectively. Vermiculite samples with five different grain sizes were employed: 100–150, 150–200, 200–250, 250–325, and 325–400 mesh. The crude oil

employed has the following properties: density, 34.2° API (at 15.6 °C); viscosity, 8.4 cP (at 37.8 °C).

The hydrated vermiculite samples were expanded (dehydration process) by heating them at 800 °C for 30 min. The hydrophobization process was performed by heating the expanded vermiculite samples with enough carnauba wax to produce a 10% hydrophobized sample.

The samples obtained were characterized by BET surface area, by using a Micromeritics apparatus. The TG and DTA curves were obtained under nitrogen atmosphere with a heating rate of 10 °C min^{-1}, by using a TGA-7 and a DTA-2000 apparatus respectively, both from Perkin–Elmer. The X-ray diffraction patterns were obtained on a Phillips equipment, by using Cu$K\alpha$ radiation. The infrared spectra were obtained in KBr pellets, in the 4000–400 cm^{-1} range, on a Perkin–Elmer apparatus. The UV–visible studies were performed on a Bomem spectrophotometer.

The adsorption studies were performed employing two distinct approaches: (a) by using columns filled with the vermiculite matrices, and promoting the flow of the crude oil through it, and (b) by dispersion of the vermiculite samples on a oil–water emulsion (50 ppm of oil) under constant magnetic stirring. The water–oil emulsion was prepared by dispersion of the desired amount of oil on water under vigorous mechanical stirring for 1 h.

3. Results and discussion

The X-ray diffraction patterns for the hydrated, anhydrous (expanded), and hydrophobized vermiculite matrices are shown in Fig. 1. Based on the 2θ values for the 100 diffraction peak, the interlayer distances for the hydrated and anhydrous samples can be calculated as 1.34 and 0.95 nm, respectively. The observed decrease of the interlayer distance for the expanded sample can be associated with the release of water molecules observed under heating [3]. On the other hand, the hydrophobized matrix exhibits the same X-ray diffraction pattern as the expanded one. Based on this fact, it can be concluded that the hydrophobizant molecules are adsorbed on the surface of the vermiculite grains and not into the interlayer space; that is, there is no formation of an vermiculite–hydrophobizant intercalation compound.

Infrared spectra (not shown) confirm the presence of the hydrophobizant agent on the clay matrix.

The thermogravimetric and derivative curves for the hydrated, expanded (anhydrous), hydrophobized, and hydrophobized with adsorbed crude oil vermiculite samples are shown in Fig. 2. For the hydrated samples, the first and second mass-loss steps are associated with the release of physisorbed/intercalated water molecules and the water molecules due to the condensation of hydroxyl groups, respectively. As expected, for the anhydrous sample, no mass-loss step is observed. On the other hand, for the hydrophobized sample, a mass loss of 10%, due to the release of the organic moiety can be observed, in agreement with the em-
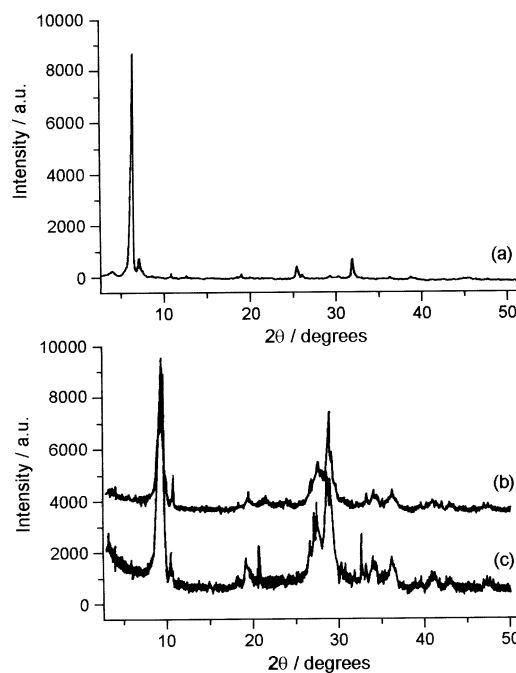

Fig. 1. X-ray diffraction patterns for (a) hydrated, (b) anhydrous, and (c) hydrophobized vermiculite samples.
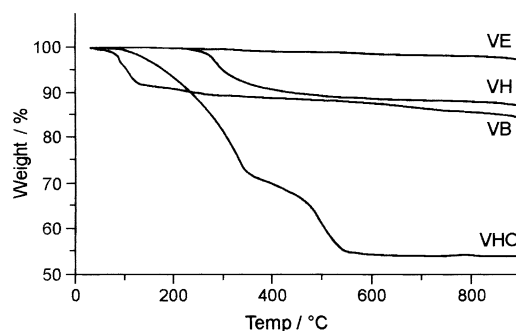

Fig. 2. Thermogravimetric curves for hydrated (VB), anhydrous (VE), hydrophobized (VH), and hydrophobized with adsorbed crude oil (VHO) vermiculite samples.

ployed hydrophobizant/clay mineral ratio. As expected, the hydrophobized sample with adsorbed crude oil exhibits the larger mass-loss percentage.

The thermogravimetric curve for the crude oil sample is shown in Fig. 3. As can be observed from Fig. 3, the crude oil exhibits four mass-loss steps. The fist one, from 25 to 220 °C is due to the release of the most volatile compounds of the oil. The second (230–350 °C), third (350–510 °C), and fourth (600–950 °C) mass-loss steps are due to the release of the heavier compounds of the oil sample. As can be observed in Fig. 2, the hydrophobized vermiculite sample with adsorbed crude oil exhibits a TG curve with a similar profile, showing the release of adsorbed oil, as well as hydrophobizant agent molecules in the temperature range considered. For all studied samples, each mass-loss step observed in the thermogravimetric curves is associated
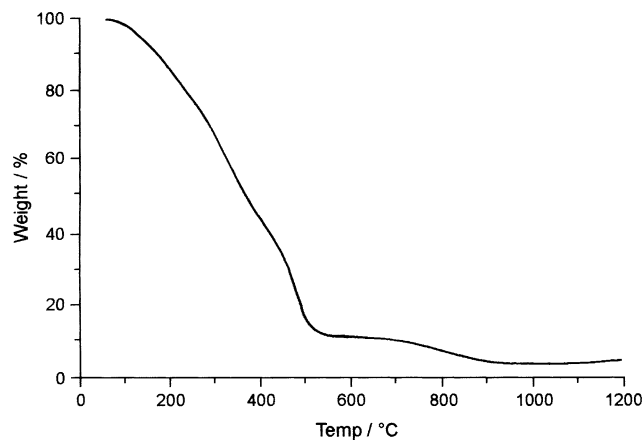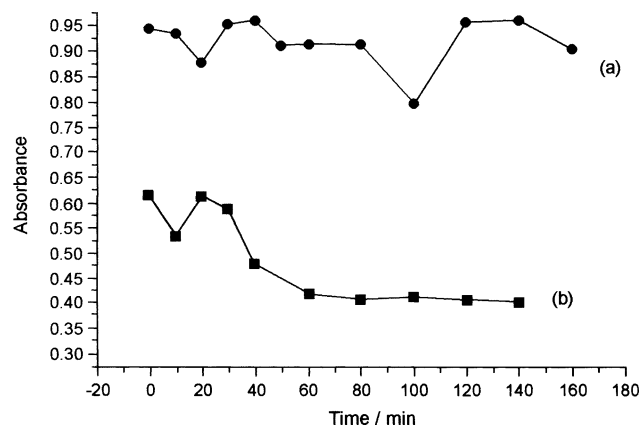
Fig. 3. Thermogravimetric curve for crude oil.

Fig. 4. UV–visible spectroscopic results for the adsorption of crude oil from a water–oil emulsion on (a) anhydrous and (b) hydrophobized vermiculite samples.

Table 1
Results for adsorption of crude oil on expanded and hydrophobized vermiculite samples

Sample	Grain size (mesh)	Surface area ($m^2\,g^{-1}$)	AF
VE	150–200	3.14 ± 0.01	0.7 ± 0.1
VE	200–250	4.05 ± 0.03	0.7 ± 0.1
VE	250–325	3.65 ± 0.02	0.8 ± 0.1
VE	325–400	7.30 ± 0.10	0.8 ± 0.1
VH	100–150	–	0.8 ± 0.1
VH	150–200	0.94 ± 0.04	0.9 ± 0.1
VH	200–250	0.97 ± 0.06	0.9 ± 0.1
VH	250–325	0.63 ± 0.06	1.0 ± 0.1
VH	325–400	1.97 ± 0.05	1.1 ± 0.1

with a respective endothermic peak in the DTA ones, which confirms the endothermic nature of the desorption processes.

The results for the adsorption of crude oil performed on columns and the BET surface area for the samples are summarized in Table 1. The adsorption factor (AF) is defined here as (oil mass)/(vermiculite mass). For both expanded and hydrophobized vermiculite samples, the adsorption studies were performed by using two different mass values: 2.0 and 4.0 g. However, it was verified that the AF values are not affected by the employed vermiculite mass. The adsorption experiments were also performed for the hydrated (not expanded) vermiculite sample, and it was observed that the AF for these samples is very low (0.3). All adsorption experiments were performed in triplicate, and it was verified that the results obtained are reproducible.

As can be observed from Table 1 data, the hydrophobized samples exhibit very high AF factors, when compared with the expanded ones. Such a fact can be, of course, attributed to the presence of the organic hydrophobic moiety, which has a high affinity toward other hydrophobic compounds or mixtures, such as crude oil.

For the adsorption studies performed on the water–oil emulsion, UV–visible spectroscopy was employed to compare the AF for the expanded and hydrophobized vermiculite samples. The results are summarized in Fig. 4. As can be

verified, the hydrophobized sample exhibits a large adsorption capacity, since the absorbance of oil on the emulsion is lower. Furthermore, it is observed by inspection of Fig. 4 data that, after 60 min, an equilibrium state is achieved, with the saturation of the solid matrix.

In general, it is observed that the AF increases with an increase of the BET surface area.

4. Conclusion

Based on the experimental data obtained it can be concluded that hydrated vermiculite exhibits a very low adsorption capacity against crude oil. On the other hand, anhydrous (expanded) and hydrophobized matrices show a high adsorption capacity. The 10% hydrophobized matrix shows a 50% increased adsorption capacity, in comparison with the expanded one. For adsorption performed in a water–oil emulsion (50 ppm of oil), saturation of the solid hydrophobized matrix is achieved after 60 min.

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