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PREPARATION AND CHARACTERIZATION OF ORGANOMONTMORILLONITE MODIFIED WITH ALKYLAMMONIUM CATION SURFACTANT: ADSORPTION EFFECT OF ZENONE

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Abstract : Montmorillonite (MMT) has been subjected to modification through ion-exchange reaction by hexadecyltrimethylammonium chloride (CTAC) ($[(C_{16}H_{33})N(CH_3)_3]Cl$). The organomodified montmorillonite (OMM) was characterized by FT-IR, XRD, ATG, SEM, EDX, and Nitrogen adsorption measurements (BET). The basal spacing of unmodified bentonite, determined by XRD was 13.54 Å and after modification it increased up to 19.74 Å. FTIR and TG/DTG results showed a good amount of organic compound in organo-modified MMT. Results of the SEM study revealed a tendency towards lump formation and agglomeration of the organomodified clay particles of montmorillonite. The adsorption of Zenone (ZE), a mycotoxin from animal food, onto MMT and OMMT was investigated. Effects of alkylammonium Cation Surfactant in binding ZE were studied. The intercalation of MMT with CTAC, the OMMT exhibited the highest adsorption rate of ZE (94.1%) which was much higher than that of MMT (11.21%). The adsorption isotherm parameters were calculated by using the Langmuir and Freundlich models and the data fitted better to the first one. All results indicate that OMMT has great potential to be a high-performance material to control ZE contamination.

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Keywords: Montmorillonite; Organo-montmorillonite; Zenone; Mycotoxins; Adsorption; Isotherm.

Introduction

The organo-modified clays have attracted a great deal of attention because of their wide applications in science and industry such as environmental researches, drug delivery and personal care and preparation of advanced materials (optical, electronic, nanocomposites).[1] Organoclays studies paid attention to swelling clay minerals, mostly smectites, because of their special physicochemical properties including their high cation exchange capacity, high surface area and consequential strong adsorption capacities.[2]

Montmorillonite (MMT) is a clay belonging to the smectite clay group characterized by a 2:1 structure with one octahedral sheet of Al^{3+} grid sandwiched between two tetrahedral sheets of Si^{4+} (Figure 1).[3] Isomorphic substitutions within the octahedral sheets produce a net negative surface charge. This negative charge is balanced by the presence of replaceable cations (Ca^{2+}, Na^{+}, etc.) in the lattice structure, which enhances the adsorption of organics contaminants.[4] Basically, the modification reactions are accomplished by replacing the interlayer cations with other species, changing the surface and structural characteristics of the clay. Large organic cations (cationic surfactants) like $(CH_3)_3N^+$ R (where R is a long alkyl hydrocarbon) occupy the exchange sites of the MMT clay and hence the surface area is increased.[5,6] These organic cations render the clay mineral hydrophobic at the surface while also increasing its wettability and thermodynamically favorable interactions with organic molecules.

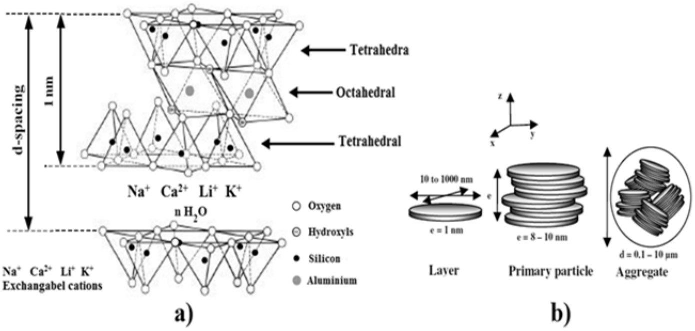


Figure 1. Montmorillonit: a) Crystalline structure and b) Microstructure.

MMT has been widely used in industry and agriculture, particularly in the adsorption of mycotoxins.[7] According to the Food and Agriculture Organization (FAO), 25% of the world's cereal grain production is contaminated by mycotoxin.[7] Zenone (ZE), a mycotoxin commonly found in animal feeds, can cause serious health problems in livestock.[8] ZE is most notorious for its effects on precocious development of mammae and other estrogenic effects in young gilts.[9] The chemical structure of ZE is presented in Figure 2. It has been reported that natural Mt are effective in adsorbing aflatoxins in vitro and in vivo.[10] However, their hydrophilic negatively charged surfaces are less effective in binding other mycotoxins, which are more hydrophobic, such as ZE. According to some literatures, organic modification of clays with organic cations, surfactants, can result in high affinity for in vitro adsorption of hydrophobic ZE.[11]

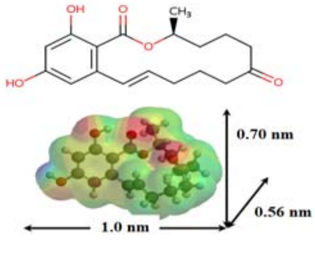


Figure 2. Chemical structure and surface electrostatic potential map of Zenone (ZE).

In the present study, MMT was modified by CTAC ($[(C_{16}H_{33})N(CH_3)_3]Cl$). MMT and organomodified montmorillonite (OMMT) were characterized by FT-IR, XRD, ATG, SEM, EDX, and

Nitrogen adsorption measurements (BET). The objective of the research is to investigate the adsorption of ZE onto the MMT clay intercalated with alkylammonium cation and explore the optimum binding of ZE.

Materials and Methods

Materials

Natural montmorillonite (MMT) was supplied by the County of Maghnia, Western Algeria. Hexadecyltrimethylammonium Chloride (CTAC) ($[(C_{16}H_{33})N(CH_3)_3]Cl$) as organo-modification was obtained from Alfa Aesar, Zenone (ZE) which was purchased from Sigma-Aldrich.

The chemical analysis was performed by X-ray fluorescence (XRF) spectroscopy on ElvaX Pro (Elvatech) spectrometer.

Montmorillonite pre-treatment

50 g of MMT were placed in 750 mL vessel with distilled water and stirred for 2 h. The suspension was decanted and separated by centrifugation. This procedure was repeated four times. Finally, the precipitate (MMT) was dried in an oven at 120 °C for 24 h and crushed. The chemical composition of dried sample is given in table 1.

Table 1. Chemical composition (wt %) of initial MMT according to XRF analysis.

Others	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	SO_3	K_2O	MnO	ZrO_2	CaO
Balance	71.60	12.75	10.77	1.66	0.70	0.09	0.09	0.02	0.04	0.31

Organomontmorillonite (OMMT) preparation

The OMMT was prepared by cation exchange reaction between the cation of the MMT and modifying agent (CTAC). Typically, 100g of MMT was suspended into 600 mL distilled water and stirred for 1h at 75 °C. Then clay suspensions were dropwise slowly added into the modifying agent (34.4 g CTAC + 200 mL distilled water heated at 75 °C), the mixture was stirred vigorously for 2 h at 75 °C. The OMMT was separated by centrifugation (4000rpm, 7min). After, that, the precipitate was collected on a filter paper, washed three times with distilled water at 65 °C till the complete elimination of chloride ions (test with $AgNO_3$ solution). The precipitate was dried to obtain a modified montmorillonite with CTAC (OMMT).

Adsorption Studies

The method of enzyme linked immunosorbent assay (ELISA) was adopted to measure the amount of ZE which was purchased from Sigma-Aldrich, ELISA kits were purchased from R-Biopharm. Firstly, ZE stock solution (4 μg/mL) was prepared, 10mg of OMMT was added to tube that was filled with 10mL ZE solution (4 μg/mL) whose pH was adjusted to 2 by adding 0.1M phosphate buffer as required. After 1 h reaction at 37 °C in temperature-controlled shaking water bath pot at a shaking rate of 120 rpm, the tube was centrifuged for 10min at 5000 rpm and then the amount of ZE remaining in the supernatant layer of suspension was analyzed by ELISA. The adsorption capacities were calculated from the difference between initial and equilibrium concentrations of ZE. For isotherm tracing, MMT (10 mg) was added to 10 mL solutions (pH = 2, 37 °C) containing different ZE concentrations (0.25, 0.5, 1.0, 2.0, 4.0, and 6.0 μg/mL). The OMMT sample was treated in a similar manner, but in this case the concentrations of ZE solutions were 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0 μg/mL. The adsorption data were fitted to the Langmuir and Freundlich isotherms models.

Characterization

FTIR spectra of MMT and OMMT were achieved on a Fourier Transformation IR Spectrophotometer type Shimadzu FTIR-8300 in the range of 400-4000 cm^{-1}, using the KBr disc preparation method.

X-ray diffraction (XRD) measurements were carried out Philips diffractometer (PW-1710). using a CuKα ($\lambda = 1.54$ Å) radiation source accelerated at 40 kV and 30 mA at room temperature. All scans were performed in 2θ range 2–20 degrees with scan speed: 2 deg/min.

Chemical analysis was performed by X-ray fluorescence (XRF) spectroscopy on ElvaX Pro (Elvatech) spectrometer.

The morphology of the samples surfaces were investigated using scanning electron microscopy (SEM) (JSM-5900 LV).

The specific BET surface area was measured at 77 K using liquid N_2 adsorption (Micromeritics - TriStar 3020 Gas Adsorption Analyzer).

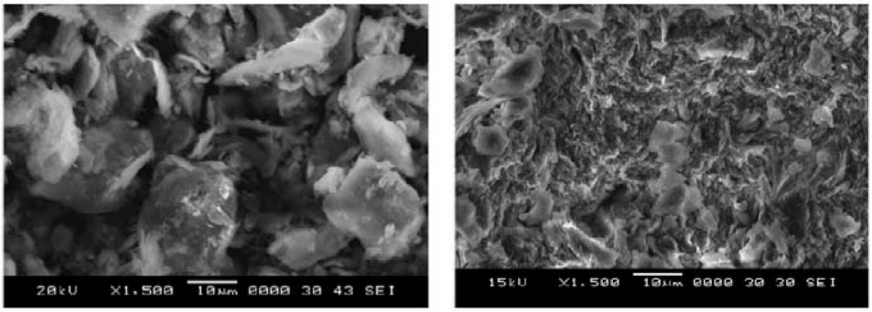
Thermal gravimetric analysis (TGA) was conducted on a Shimadzu TGA - 51H analyser with temperature program = heat from 30 °C to 900 °C; heating rate of 10°C/ min in Nitrogen atmosphere with a purge rate of 20 mL/min.

Results and Discussion

Characterization of Sorbent

Scanning Electron Microscope (SEM) Analysis

The surface morphology of both, MMT and the OMMT is illustrated in Figure 3. MMT shows a massive and aggregated morphology. The presence of the alkylammonium cation expands the clay structure, which exhibits a more open morphology, while individual blocks of layers can be distinguished in it (Figure 3b).



(a) (b)

Figure 3. SEM micrographs of : (a) MMT (b) OMMT.

IR spectroscopy

FTIR spectra of MMT and OMMT are shown in Figure 4. As noted, all the spectra show bands at 3636 and 3395 cm^{-1} attributed to O–H stretching for the silicate and water, respectively, 1639 cm^{-1} (related to O–H bending), 1040 cm^{-1} (owing of stretching vibration of Si–O–Si from silicate), 917 cm^{-1} (from Al–OH–Al deformation of aluminates), and 524 and 472 cm^{-1} (Al-O stretching and Si-O bending vibrations of MMT, respectively).[12] However, there are some bands in OMMT spectra which are not exhibited by the MMT; these bands were located at 2924, 2842 and 1475 cm^{-1} and were assigned to C–H vibrations of methylene groups (asymmetric stretching, symmetric stretching and bending, respectively) from chemical structure of the surfactant.[13]

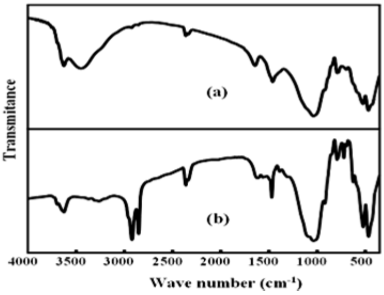


Figure 4. FTIR spectra of: a) MMT and b) OMMT.

XRD analysis

The X-ray spectra for powder MMT, and OMMT are shown in Figure 5. Bragg's equation, $2\,d_{001}\sin\theta = n\lambda$, was used to calculate the basal spacing of the OMMT as well as the MMT. The characteristic d_{001} diffraction peak for MMT in the 2θ region is located at 6.52°, d_{001} = 13.54 Å. The modification of the MMT with HTACl shifts the d_{001} peak to lower values in the 2θ region, which are located at 4.51°, d_{001} = 19.74 Å for OMMT. This shift indicates an increase in the basal spacing of the silicate platelets, due to the penetration and grafting of the quaternary salt via ion exchange to the clay platelets. The indexing of the d_{001} peak in the diffraction patterns of modified clays also suggests that the morphology of the clays is intercalated.[14]

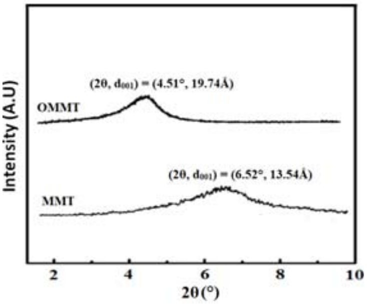


Figure 5. XRD pattern of MMT and OMMT.

Thermogravimetric analysis (TGA)

The TGA curves MMT and OMMT are shown in Figure 6. MMT displays two thermal degradation transitions. The first one occurs in the temperature range 100–350 °C and is due to the vaporization of both the free water (i.e., the water sorbed on the external surfaces of crystals) and the water residing inside the interlayer space, forming hydration spheres around the exchangeable cation.[12] The second transition takes place at higher temperatures (between 500 and 800 °C) and is owing to the structural water resulting from the dehydroxylation of clay OH units. On the other hand, OMMT follows a fourstep decomposition process. The vaporization of free water takes place at temperatures below 200°C, while the surfactant's decomposition happens in the temperature between 200–500°C. Dehydroxylation of the aluminosilicates occurs between 500 and 800 °C.[14]

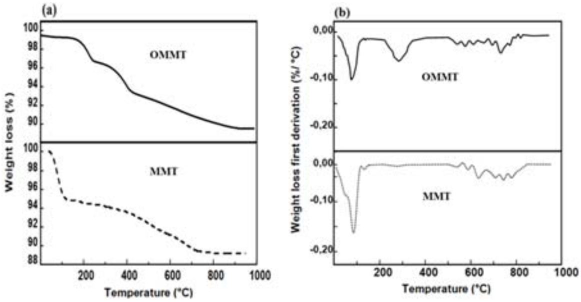


Figure 6. TGA (**a**) and DTGA (**b**) curves of: MMT and OMMT.

BET

The specific surface area and pore size distribution were determined by nitrogen adsorption isotherms for both MMT and OMMT were shown in Figure 7. Both MMT and OMMT have mesoporous structures. Mesoporous structure was shown by a hysteresis between adsorption and desorption curve after relative pressure (P/P_0) of 0.4. The difference between MMT and OMMT lies on its volumetric adsorption capacity (V_{ads}) and BET surface area.

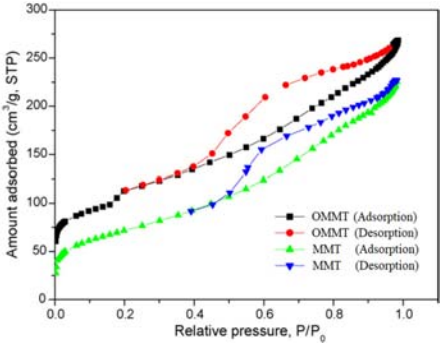


Figure 7. Nitrogen adsorption/desorption isotherms MMT and OMMT at 77K.

OMMT had larger Vads than MMT (0.75 cm^3/g vs 0.51 cm^3/g) but lower surface area (101 m^2/g vs 119 m^2/g) which indicates the formation of larger pore on OMMT as compared to MMT due to HTACl insertion MMT interlayer.

Adsorption Isotherms

It is important to analyze the isotherm data so as to investigate the mechanism of ZE adsorption by MMT and OMMT, and the results can help realize better design to remove ZE from the foods for human and animal. Therefore, two main models of adsorption isotherm were analyzed at pH = 2, Langmuir and Freundlich, respectively.

The linearized form of Langmuir can be written as follows:[15]

$$\frac{C_e}{q_e} = \frac{1}{(q_m \times K_L)} + \frac{C_e}{q_m} \tag{1}$$

where q_e (mg/g) is the equilibrium adsorption capacity, Ce is the equilibrium concentration of ZE in solution (mg/L), K_L is the equilibrium adsorption constant related to the affinity of binding sites (mg/L), and q_m is the maximum amount of ZE per unit weight of adsorbent for complete monolayer coverage (mg/g).

Secondly, the adsorption data were fitted to the linear form of Freundlich adsorption model:[16]

$$log\, q_e = log\, K_F + \frac{1}{n_F} log\, C_e \tag{2}$$

where q_e and Ce are defined as above, K_F is the Freundlich constant representing the adsorption capacity (mg/g), and n_F is the heterogeneity factor depicting the adsorption intensity. Freundlich equation is an exponential variation in site energies and it is assumed that the adsorbent has heterogeneous energy distribution of active sites. Theoretically, Freundlich model is suitable for use with heterogeneous surfaces and with this expression; an infinite amount of adsorption can occur.

Table 2. Isotherm parameters for ZE adsorption onto MMT and OMMT.

Sample	Langmuir isotherm constants			Freundlich isotherm constants		
	q_m (mg/g)	K_L (L/g)	R^2	n_F	K_F	R^2
MMT	0.473	4.127	0.999	3.925	0.418	0.882
OMT	5.862	6.823	0.998	1.952	3.682	0.823

The absorption isothermal curves (Figure 8) and all isotherm values (table 2) display that the data of MMT fit to the Langmuir model much better (R^2 = 0.999), whereas the Freundlich model is less appropriate (R^2 = 0.882); meanwhile, comparing the R^2 values of OMMT, the Langmuir model obtains much better fit too, indicating that isotherms of both MMT and OMMT are consistent with the Langmuir model and conform to monolayer adsorption over a homogenous adsorbent surface. The results show that organic intercalation does not change the adsorption mode. The qm values of MMT and OMMT shown in Table 3 present that the adsorbance of ZE on OMMT is higher than that of MMT; it indicates that interlayer ions of HTACl in OMMT have stronger interaction with ZEA than that of inter layer cations in MMT.

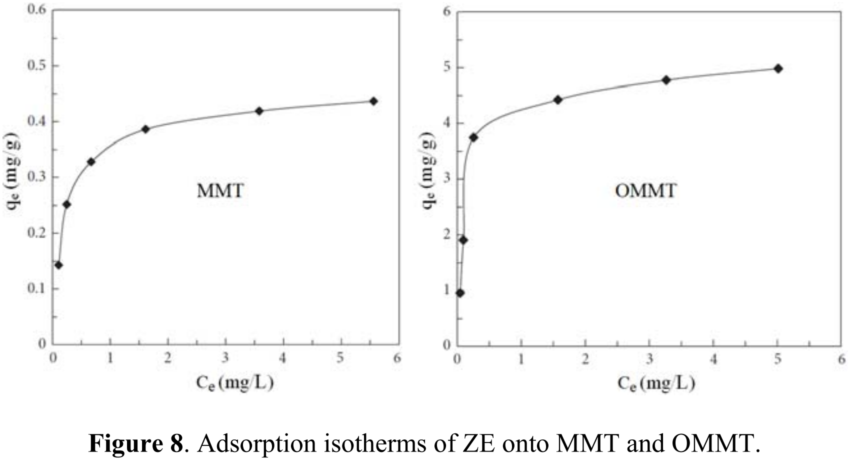


Figure 8. Adsorption isotherms of ZE onto MMT and OMMT.

Conclusions

MMT has been successfully modified using HTACl cationic surfactant. As the FTIR spectroscopy indicated the organic compound in organo-modified sample, the XRD pattern presented increasing in d-spacing and enlarging the interlayer space in OMMT. The TGA and DTGA curves for OMMT show the degradation due to residual water desorption, dehydration, followed by decomposition of the organic modifier and the dehydroxylation of the organo–montmorillonite. No great morphological changes had been recognized on SEM images. The results demonstrate the adsorption of ZE onto MMT and OMMT. An effective adsorbent of OMMT for removing ZE, which exhibited the highest adsorption rate of ZEA (94.1%). According to the analysis of results, it can be concluded that the higher adsorption capacity of ZE on OMMT mainly lies in the factors of greater surface area, higher porosity, much more active sites, and hydrophobicity. Determination of ZE adsorption isotherms for MMT and OMMT shows that the ZE adsorption follows the Langmuir isotherm model and the maximum adsorbance of ZE on adsorbents was estimated to be 5.862 mg/g.

Generally speaking, in the practical application, detoxification treatments with OMMT are technically and economically reliable, including (1) the elimination of ZE, (2) not having any secondary pollution, (3) the protection of nutritive value, and (4) the antibacterial activity. Meanwhile, this adsorbent is cost effective and has high removal efficiency for ZE from aqueous and organic solutions. Furthermore, the adsorbent is adaptable and stable when applied in different environments, which are the most critical properties for the removal of ZE with variant concentrations in natural contaminated food.

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