Research Article

Preparation and Characterization of Montmorillonite Intercalation Compounds with Quaternary Ammonium Surfactant: Adsorption Effect of Zearalenone

Yujin Li, 1 Lu Zeng, 2 Yan Zhou, 1 Tiefu Wang, 1 and Yanji Zhang 1

1 College of Earth Sciences, Jilin University, Changchun 130000, China
2 College of Materials Science and Engineering, Chongqing University, Chongqing 400030, China

Correspondence should be addressed to Lu Zeng; zoool@foxmail.com

Received 24 September 2013; Accepted 14 December 2013; Published 9 February 2014

Academic Editor: Sun-Hwa Yeon

Copyright © 2014 Yujin Li et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Montmorillonite (Mt) was used as the original material to prepare intercalation compounds with quaternary ammonium surfactant (QAS). The adsorption of zearalenone (ZEA) onto Mt and organomodified Mt was investigated in vitro. Effects of QAS in binding ZEA were studied. By the method of intercalation with dioctadecylmethylbenzylammonium chloride (DOMBAC), the sample exhibited the highest adsorption rate of ZEA (93.2%) which was much higher than that of Mt (10.5%). Several methods were adopted to characterize samples, including XRD, TG/DSC, N2 adsorption/desorption, and FTIR. Adsorption isotherm parameters were obtained from Langmuir and Freundlich and the adsorption data fitted better to Langmuir. All results indicate that organomodified Mt has great potential to be a high-performance material to control ZEA contamination.

1. Introduction

Many types of clay minerals such as montmorillonite (Mt), sepiolite, and kaolinite have shown high adsorption capacity. Mt, a clay mineral with 2:1 layered structure, can hold some cations between its layers. Substitution of Si4+ with Al3+ in tetrahedral sheets and Al3+ with Mg2+ in octahedral sheets make the lattice a net negative charge which is usually balanced by cations of Li+, Na+, and Ca2+ located between the layers. These cations can be easily replaced by other organic or inorganic cations under certain conditions, which endow Mt with some special properties [1]. Mt has been widely used in industry and agriculture, particularly in adsorption of mycotoxins. According to the Food and Agriculture Organization (FAO), 25% of the world’s cereal grain production is contaminated by mycotoxins [2]. Zearalenone (ZEA), along with others most of mycotoxins, commonly found in animal feeds, can cause serious health problems in livestock [3, 4]. Zearalenone is most notorious for its effects on precocious development of mammae and other estrogenic effects in young gilts [5]. The chemical structure of ZEA is presented in Figure 1 [6]. It has been reported that natural Mt are effective in adsorbing aflatoxins in vitro and in vivo [7, 8]. However, their hydrophilic negatively charged surfaces are less effective in binding other mycotoxins, which are more hydrophobic, such as ZEA. According to some literatures, organic modification of clays with organic cations, surfactants, can result in high affinity for in vitro adsorption of hydrophobic ZEA [4–9].

The quaternary ammonium surfactant (QAS) is the most commonly used organic modifier, which can enhance the lipophilicity of Mt. However, QAS contains many different kinds such as the types with short carbochain, medium carbochain, long carbochain, and double carbochain and the type with functional group of benzyl. In this study, Mt intercalation compounds with QAS were prepared and characterized; the adsorption effect of ZEA onto adsorbents was compared. The objective of the research is to investigate
the adsorption of ZEA onto Mt intercalation compounds with QAS and explore the optimum QAS in binding ZEA. To the best of our knowledge similar research has not been reported.

2. Materials and Methods

2.1. Preparation and Characterization of Mt. Mt, the original materials supplied by Sanding Company, consists of a lot of Mt and a small amount of quartz, according to powder X-ray diffraction (XRD) analysis shown in Figure 2. The primary ion in the exchangeable position is sodium and the cation exchange capacity of Mt is 1.44 mmol/g [10]. Mt was dried at 80°C under vacuum for 8h at 110°C. Infrared spectra were recorded by means of Thermoelectron FTIR spectrometer (Avatar370) in the range of 4000–400 cm⁻¹.

2.2. Adsorption Experiments. The method of enzyme linked immunosorbent assay (ELISA) was adopted to measure the amount of ZEA which was purchased from Sigma-Aldrich Co., and ELISA kits were purchased from R-Biopharm Co. Firstly, ZEA stock solution (4 µg/mL) was prepared, then 10 mg of organomodified Mt was added to tube that was filled with 10 mL ZEA solution (4 µg/mL) whose pH was adjusted to 2 by adding 0.1 M 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 10 min at 5000 rpm and then the amount of ZEA remaining in the supernatant layer of suspension was analyzed with the method of ELISA. The adsorption capacities were calculated from the difference between initial and equilibrium concentrations of ZEA. For isotherm study, Mt (10 mg) was added to 10 mL ZEA solution (pH = 2, 37°C) at different concentrations (0.25, 0.5, 1.0, 2.0, 4.0, and 6.0 µg/mL) and so was organomodified Mt but with increased concentrations of ZEA solution (1.0, 2.0, 4.0, 6.0, 8.0, and 10.0 µg/mL, resp.) due to its higher adsorbance of ZEA. The adsorption data were fitted to the models of Langmuir and Freundlich isotherm.

3. Results and Discussion

3.1. Effects of QAS. As can be seen from Table 1, Mt is quite ineffective in adsorbing ZEA (10.5%) due to its poor lipophilicity and different kinds of QAS can draw significantly different influences on the adsorption of ZEA. For QAS without benzyl, the type with medium carbochain is beneficial to the adsorption of ZEA because MOTAC obtains the maximum adsorbance of ZEA (45.8%), which is higher than that of MDTAC (24.7%) and MBTAC (36.5%).
Table 1: Effects of QAS on the adsorbance of ZEA on adsorbents.

<table>
<thead>
<tr>
<th>Samples</th>
<th>QAS</th>
<th>Molecular structural formula of QAS</th>
<th>Initial amount of ZEA (μg)</th>
<th>Adsorption rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt</td>
<td>—</td>
<td>—</td>
<td>40</td>
<td>10.5</td>
</tr>
<tr>
<td>MDTAC</td>
<td>DTAC</td>
<td>$\text{H}<em>3\text{C} - N^+ - \text{C}</em>{12}\text{H}_{25}\text{Cl}^-$</td>
<td>40</td>
<td>24.7</td>
</tr>
<tr>
<td>MDDBAC</td>
<td>DDBAC</td>
<td>$\text{N}^+ - \text{C}<em>{12}\text{H}</em>{25}\text{Cl}^-$</td>
<td>40</td>
<td>50.8</td>
</tr>
<tr>
<td>MOTAC</td>
<td>OTAC</td>
<td>$\text{H}<em>3\text{C} - N^+ - \text{C}</em>{18}\text{H}_{37}\text{Cl}^-$</td>
<td>40</td>
<td>45.8</td>
</tr>
<tr>
<td>MODBAC</td>
<td>ODBAC</td>
<td>$\text{N}^+ - \text{C}<em>{18}\text{H}</em>{37}\text{Cl}^-$</td>
<td>40</td>
<td>69.1</td>
</tr>
<tr>
<td>MBTAC</td>
<td>BTAC</td>
<td>$\text{H}<em>3\text{C} - N^+ - \text{C}</em>{22}\text{H}_{45}\text{Cl}^-$</td>
<td>40</td>
<td>36.5</td>
</tr>
<tr>
<td>MDOMBAC</td>
<td>DOMBAC</td>
<td>$\text{N}^+ - \text{C}<em>{18}\text{H}</em>{37}\text{Cl}^-$</td>
<td>40</td>
<td>93.2</td>
</tr>
</tbody>
</table>

result is attributed to that the lipophilicity of MOTAC with longer carbochain is higher than that of MDTAC, but when the carbochain is too long, it is hard for the intercalation reaction which is adverse to the organic modification [12]. Moreover, the influence of intercalation reaction on pore size of adsorbent has two completely opposite effects [13]: the “pore blockage” effect, organic molecules fill pores and result in the decrease of pore size and $S_{\text{BET}}$, and the “pore prop” effect, macromolecular organics insert into the interlayer and cause the distraction of aluminosilicate layer and the increase of pore size and $S_{\text{BET}}$. Hence, the molecule sizes of QAS have great influences on the absorption capacity of adsorbents. Meanwhile, benzyl group has great influences on the adsorption of ZEA, which can significantly increase the adsorbance of ZEA on adsorbents. Herein, the adsorbance of ZEA on MDDBAC (50.8%) and MODBAC (69.1%) is higher than that of MDTAC and MOTAC, respectively. It can be attributed to that the critical effect of benzyl ring into the interlamellar space of Mt greatly enhances the penetration of QAS, which results in a better effect of modification; besides,
benzyl is beneficial to the increase of lipophilicity [14].
Furthermore, MDOMBAC has higher adsorption capacity of ZEA (93.2%) than that of MODBAC, which is the maximum in all of the organomodified Mt, indicating that optimal QAS with double medium carboxyl and benzyl group does favor the adsorption of ZEA onto adsorbent. The result obtained shows that QAS plays an important role in binding ZEA and it can be attributed to the physicochemical property of QAS which has influences on the dispersion and lipophilicity of organomodified Mt [15–17].

3.2. XRD Characterization. XRD patterns reveal the microstructure variety of samples. The comparative XRD patterns of Mt and MDOMBAC are presented in Figure 2. It shows that the d001 values of Mt and MDOMBAC are 1.26900 and 1.93526 nm, respectively, indicating that Mt is intercalated by dioctadecylmethylbenzylammonium (DOMBA) ions because the radius of DOMBA ions is larger than that of sodium ion [18]. Besides, there is no significant difference between their patterns, indicating that the basic structure of Mt is not changed. By the way of organic intercalation, MDOMBAC can obtain greater surface area and become more porous theoretically, which can improve its adsorption ability of ZEA greatly [19]. Therefore, the adsorption capacity of ZEA on MDOMBAC is much higher than that of Mt.

3.3. TG/DSC Characterization. The TG/DSC curves of Mt and MDOMBAC are shown in Figure 3. The DSC curves of Mt show that the first endothermic valley appears at 98.3°C for the loss of the physically adsorbed water and the second endothermic valley appears at 153.9°C corresponding to the loss of the interlayer water. About 5.3% of weight loss is shown in TG curve of Mt. With the increase of temperature, the third endothermic valley appears at 689°C with 5.26% of weight loss, which is due to the dehydroxylation. Comparatively, the TG/DSC curves of MDOMBAC show that there are only one endothermic valley at 73.1°C for the loss of physically adsorbed water and interlayer water, because of the less moisture content caused by hydrophobicity after organic intercalation. Between 400 and 700°C, a great exothermic peak appears due to the burning of organism and then a lot of heat releases and about 43.73% of weight loss occurs, which is close to the adding quantity of DOMBAC. When the temperature rises continuously, the decomposition of MDOMBAC occurs with 1.32% of weight loss [20, 21]. The results obtained show that the dosage of DOMBAC is proper and the structure of MDOMBAC is stable below 400°C, confirming that DOMBA ions added are bound in the interlayer space of MDOMBAC [22].

3.4. N2 Adsorption/Desorption. The \( S_{\text{BET}} \), \( V_{\text{total}} \), and \( D_p \) of Mt and MDOMBAC were measured, and all of the data are summarized in Table 2. The \( N_2 \) adsorption/desorption isotherms and pore size distribution curves of samples are shown in Figure 4. It shows that isotherms exhibit Type II behaviors according to the IUPAC classification [23], and the \( D_p \) of samples was about 7–9 nm, characteristics of major mesoporous adsorbents, seen from the formed hysteresis loop which fits to the fourth type of hysteresis loop (H4), indicating slit pores formed from layer structure [23]. The main differences obtained from the isotherms are that the \( S_{\text{BET}} \) and \( V_{\text{total}} \) of MDOMBAC are significantly larger than that of Mt, indicating the different pore structure of MDOMBAC with more mesoporous. It can be attributed to the "pore prop" effect; meanwhile, the incorporation of DOMBA ions and Mt in the interlayer area forms a more porous intercalation compound [24]. The results demonstrate that, with the special pore structure formed by intercalation, MDOMBAC obtains a higher adsorption capacity of ZEA than that of Mt.

3.5. FTIR Characterization. The FTIR spectra of Mt and MDOMBAC are shown in Figure 5. The spectra of Mt shows that the stretching vibration band of Al–OH–Al group at octahedral layer is at about 3668 cm\(^{-1}\) and its bending vibration band is at 915 cm\(^{-1}\). The band at around 3430 cm\(^{-1}\) is the stretching vibration of interlayer water molecule and at 1639 cm\(^{-1}\) is the bending vibration. The two bands are observed at 1077 cm\(^{-1}\) and 1031 cm\(^{-1}\) in the Si–O–Si stretching vibration region and the former is stronger; the band at 463 cm\(^{-1}\) is the bending vibration of Si–O–Si. The weak band at 525 cm\(^{-1}\) is bending vibration of Si–O–Al and the band at 834 cm\(^{-1}\) is due to stretching vibration of Al\(^{IV}\) tetrahedra, when replacing Si with Al [25]. After intercalation with DOMBAC, three new bands are observed at 1473 cm\(^{-1}\), 2921 cm\(^{-1}\), and 2852 cm\(^{-1}\) which are bending vibration, asymmetrical stretching vibration, and symmetrical stretching vibration of CH due to the introduction of DOMBA ions [26]. These results suggest that Mt and DOMBA ions have been combined together, which results in more active sites on MDOMBAC and higher adsorption capacity of ZEA.

### Table 2: The structure characteristics of Mt and MDOMBAC.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>( V_{\text{total}} ) (cm(^3)/g)</th>
<th>( D_p ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt</td>
<td>41.217</td>
<td>0.087</td>
<td>7.854</td>
</tr>
<tr>
<td>MDOMBAC</td>
<td>147.745</td>
<td>0.276</td>
<td>9.121</td>
</tr>
</tbody>
</table>
3.6. Adsorption Isotherms. It is important to analyze the isotherm data so as to investigate the mechanism of ZEA adsorption by Mt and MDOMBAC, and the results can help realize better design to remove ZEA from the foods for human and animal. Therefore, two main models of adsorption isotherm were analyzed at pH = 2, Langmuir and Freundlich, respectively [27, 28].

The Langmuir adsorption isotherm assumes that adsorption occurs at specific homogeneous sites inside the adsorbent. The adsorption data were fitted to the linear form of Langmuir adsorption model (1) and the adsorption isotherm was obtained by plotting the particular adsorption \( (C_e/C) \) against the equilibrium concentration of ZEA \( (C_e) \). \( C_e \) is the equilibrium concentration of ZEA which means the final concentration (mg/L) of ZEA in the solution after adsorbed, \( C_m \) is the maximum adsorbance of the sorbent, \( C \) is the amount of ZEA adsorbed by the adsorbent at equilibrium, and \( K \) is a Langmuir constant related to the adsorption energy:

\[
\frac{C_e}{C} = \frac{1}{C_m K} + \frac{C_e}{C_m}.
\] (1)

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

\[
\ln C = \ln K_f + \frac{1}{n_f} \ln C_e,
\] (2)

where \( K_f \) is Freundlich constant related to adsorption intensity and \( n_f \) is constant related to adsorption intensity as well; \( C \) and \( C_e \) denote adsorbance of ZEA and equilibrium concentration of ZEA, respectively. 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.

The absorption isothermal curves (Figure 6) and all isotherm values (Table 3) display that the data of Mt fit to the Langmuir model much better \( (R^2 = 0.9997) \), whereas the Freundlich model is less appropriate \( (R^2 = 0.8817) \); meanwhile, comparing the \( R^2 \) values of MDOMBAC, the Langmuir model obtains much better fit too, indicating that isotherms of both Mt and MDOMBAC 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 \( C_m \) values of Mt and MDOMBAC shown in Table 3 present that the adsorbance of ZEA on MDOMBAC is higher than that of Mt; as the type of interlayer ions is the key factor for the adsorption [29, 30], it indicates that interlayer ions of DOMBA in MDOMBAC have stronger interaction with ZEA than that of sodium ions in Mt.
4. Conclusions

The final results demonstrate the adsorption of ZEA onto Mt and organomodified Mt. By the method of intercalation with DOMBAC, an effective adsorbent of MDOMBAC for removing ZEA was prepared, which exhibited the highest adsorption rate of ZEA (93.6%). Mt and MDOMBAC were characterized by several methods, including XRD, TG/DSC, \( N_2 \) adsorption/desorption, and FTIR. According to the analysis of results, it can be concluded that the higher adsorption capacity of ZEA on MDOMBAC mainly lies in the factors of greater surface area, higher porosity, much more active sites, and hydrophobicity. Determination of ZEA adsorption isotherms for Mt and MDOMBAC shows that the ZEA adsorption follows the Langmuir isotherm model and the maximum adsorbance of ZEA on adsorbents was estimated to be 5.0761 mg/g.

DOMBAC can be used as the potential adsorbent to prevent mycotoxicosis.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The study was supported by the Research Funds for the Geologic Survey (1212011120277).

References


