

Title: Selecting and modifying clays to enhance their adsorption for zearalenone

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Abstract: Zearalenone (ZEN) is one of the five major groups of agriculturally important mycotoxins produced by *Fusarium* mold. These mycotoxins occur frequently on corn, wheat, barley, oat, tree nuts, rice, peanut, sorghum, hay, fruits, and other crops. The Food and Agriculture Organization (FAO) of the United Nations estimates that 25% of the world's food crops are affected by mycotoxin producing fungi and that a nearly one billion tonnes of foodstuffs loss due to mycotoxins occurs every year. Minimizing the health risks and economic losses from mycotoxin contamination are crucial issues. Inspired by reported high adsorption capacity of many smectites for aflatoxins and the similarity in molecular weight, functional groups, and polarity between aflatoxins and zearalenone, we aimed to select and modify clay minerals to detoxify/decontaminate this mycotoxin by adsorption.

We used three approaches to modify the interlayer surface polarity of smectites on the nanometer scale: 1) Selecting smectites with different layer charge densities. Six smectites with different layer charged densities were chosen in this study to evaluate their adsorption capacities for zearalenone. 2) Replacing the interlayer cations in smectites with different hydration energy and valences. By varying the exchange cations and the layer charge density, the space between the hydrated cations were varied to match the size of the targeted mycotoxins, 3) Characterizing smectite-mycotoxin complexes. Once the optimum conditions for smectite-zearalenone interactions were identified, zearalenone-smectite complex was synthesized and characterized with variable-temperature X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The XRD and FTIR data were used to verify if interlayer adsorption occurred on smectites and the bonding mechanisms between zearalenone and smectites.

Experimental results indicated that smectites with CEC ranging from 107.7 to 136.6 cmol/kg showed higher adsorption capacities, i.e. 0.055 mol/kg (1.78% by weight) for zearalenone. Among eight different interlayer cations saturation, monovalent cations saturated smectites showed higher adsorption capacities than divalent cations saturated smectites. The highest adsorption capacity was Na-clay, i.e. 0.111 mol/kg (3.50% by weight). In FTIR characterization, the results confirmed the presence of strong interaction between both zearalenone and the smectite. This indicated the stability of the adsorbed zearalenone as the samples were washed twice with water. The X-ray diffraction of Li-clay suggested the interlayer adsorption of zearalenone which was confirmed by heating the sample at high temperature. On the other hand, the interlayer adsorption of zearalenone was not observed in Mg-clay by the XRD result. The mechanism of the Mg-clay adsorption needs further study. Overall, the preliminary results indicated that the zearalenone adsorption capacity can be enhanced with changing layer charge densities of smectite and changing their interlayer cations. The adsorption mechanism was interlayer adsorption. Yet, the results also suggested that it is possible to enhance the adsorption by modifying the adsorbing environment on a nanometer scale.