

EFFECTS OF METHOD OF CLAY PREPARATION ON SUBSEQUENT ADSORPTION OF THE INSECTICIDE FENSULFOTHION

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The manner in which montmorillonite and illite adsorbents were prepared for batch-type adsorption experiments determined the extent of fensulfothion (Dasanit®) adsorption. Curve-fitting techniques produced regression equations for the isotherms generated by four clay systems (Na- and Ca-montmorillonite and illite) and by the four preparation treatments per system (freeze-dried; freeze-dried, resuspended; freeze-dried, 100% RH; suspension). Only the regression equation isotherms of the Na-illite system and one treatment comparison of the Ca-illite system (freeze-dried, 100% RH vs. suspension) were not significantly different (5% level). In general, the freeze-drying process increased fensulfothion adsorption relative to that for the same clay in suspension. Conditioning freeze-dried clay with water vapor (100% RH) prior to adsorption decreased fensulfothion adsorption relative to the freeze-dried clay (dried over P_2O_5).

Le mode de préparation des adsorbants de la montmorillonite et de l'illite pour des expériences d'adsorption discontinue a déterminé le degré d'adsorption du fensulfothion (Dasanit®). Les techniques d'ajustement des courbes ont donné des équations de régression pour les isothermes engendrées par quatre systèmes argileux (montmorillonite et illite-Na et Ca) et par les quatre modes de préparation pour chaque système (lyophilisation; lyophilisation et remise en suspension; lyophilisation et stabilisation à 100% d'humidité relative; suspension). Seules les isothermes de l'équation de régression du système illite-Na et d'une comparaison d'un mode du système illite-Ca (lyophilisation et stabilisation à 100% d'humidité relative contre suspension) n'ont pas été significativement différentes ($P < 0.05$). En général, le processus de lyophilisation a accru l'adsorption du fensulfothion par rapport à celle de la même argile en suspension. Le conditionnement de l'argile lyophilisée à la vapeur d'eau (humidité relative 100%) avant l'adsorption a diminué l'adsorption du fensulfothion par rapport à celle de l'argile lyophilisée (séchée sur P_2O_5).

There are two basic approaches to conducting batch-type adsorption studies in aqueous clay or soil suspensions: (a) to add the adsorbate solution to a suspension of the adsorbent (Brindley et al. 1963; Frissel 1961; Weber 1970); or (b) to add the adsorbate solution directly to the dried adsorbent. The dried adsorbents have been prepared in a number of ways including air-drying (Adams and Li 1971; Boucher and Lee 1972), freeze-drying (Bailey et al. 1968; Lotse et al. 1968) and oven-drying (Mills and Biggar 1969; Yaron and Saltzman 1972). Prior to the experiments, some dried adsorbents have been equilibrated under vacuum over anhydrous P_2O_5 (Bailey et al. 1968; Yaron and Saltzman 1972).

During recent adsorption studies on the fensulfothion—montmorillonite system (Bowman 1973), it was observed that the addition of the fensulfothion solution to freeze-dried montmorillonite produced an adsorption isotherm which was positioned to the left (lower equilibrium concentrations, greater adsorption) of the isotherm produced by adding the fensulfothion solution to a montmorillonite suspension (all other parameters identical). It was unknown whether the increased fensulfothion adsorption by the freeze-dried montmorillonite could be attributed to competitive effects between water

and fensulfothion molecules, or whether the freeze-drying process had altered the clay surface. The purpose of this study was to investigate the effects of several pretreatments for montmorillonite and illite clays upon subsequent fensulfothion adsorption.

MATERIALS AND METHODS

The < 2- μm fraction of montmorillonite no. 25 (Wyoming bentonite) and the 2- to 20- μm fraction of illite no. 36 (Fithian, Illinois), from Ward's Natural Science Establishment, were saturated with either Na^+ or Ca^{2+} as described previously (Bowman 1973). The bulk of these two clays fall into these respective particle size ranges. Following saturation, each clay was divided into four portions for adsorption studies: (a) one portion was freeze-dried, and 450-mg samples were weighed into adsorption bottles and equilibrated over anhydrous P_2O_5 until used, (b) one portion was freeze-dried, and resuspended in distilled water (30 mg/ml) and 15-ml aliquots were pipetted into adsorption bottles, (c) one portion was freeze-dried, and 450-mg samples were weighed into adsorption bottles and equilibrated at 100% RH, and (d) one portion was put into suspension (30 mg/ml) and 15-ml aliquots were pipetted into adsorption bottles. The adsorption isotherms were generated as reported previously (Bowman 1973), by mixing 15 ml of fensulfothion solution and 15 ml of clay suspension. In experiments using the freeze-dried clay, 30 ml of aqueous fensulfothion solution were pipetted into the adsorption bottles containing the 450 mg (oven-dry basis) of freeze-dried clay. The analytical procedures for fensulfothion were the same as reported previously (Bowman 1973).

RESULTS

Figures 1–4 show the fensulfothion adsorption isotherms for the Na– and Ca-montmorillonite and illite systems, as affected by the clay preparation technique. Using a curve-fitting computer program, various curvilinear regression equations were tested for their correspondence to the experimental isotherms. Regression equations including the \log_e (Ln) transformation of both Y (dependent variable, x/m , amount of fensulfothion adsorbed/unit weight of clay) and X (independent variable, C_e , $\mu\text{g}/\text{ml}$) gave the best fit.

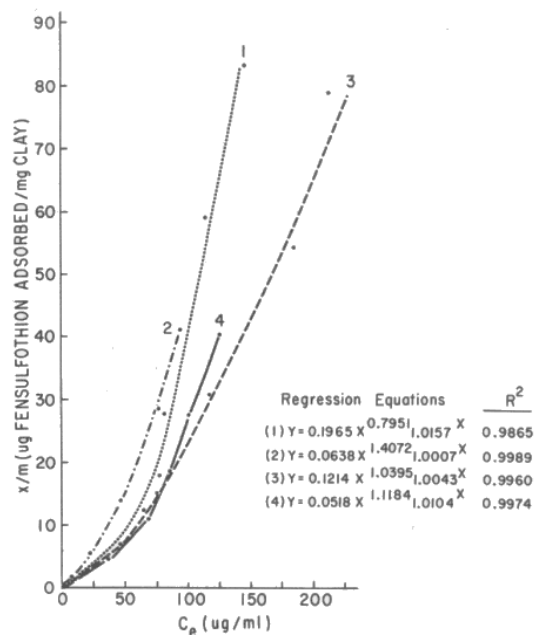


Fig. 1. Adsorption isotherms for the fensulfothion-Na-montmorillonite system: (1) freeze-dried; (2) freeze-dried, resuspended; (3) freeze-dried, 100% RH; (4) suspension.

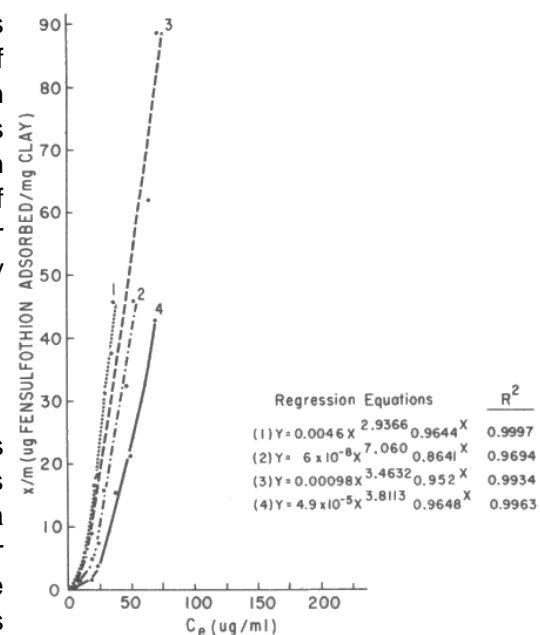


Fig.2. Adsorption isotherms for the fensulfothion-Ca-montmorillonite system: (1) freeze-dried; (2) freeze-dried, resuspended; (3) freeze-dried, 100% RH; (4) suspension.

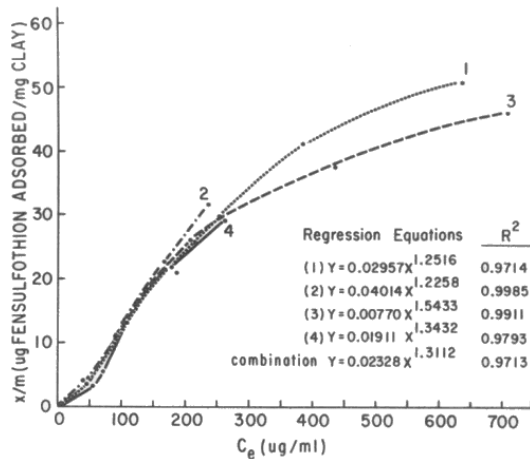


Fig.3. Adsorption isotherms for the fensulfothion–Na–illite system: (1) freeze-dried; (2) freeze-dried, resuspended; (3) freeze-dried, 100% RH; (4) suspension.

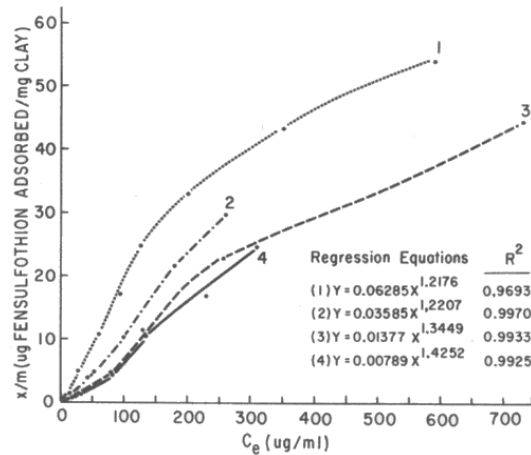


Fig. 4. Adsorption isotherms for the fensulfothion–Ca–illite system: (1) freeze-dried; (2) freeze-dried, resuspended; (3) freeze-dried, 100% RH; (4) suspension.

The equations selected for statistical comparisons were those with the highest R^2 for all treatments, and therefore not necessarily the best fit for any individual treatment. The 5% significance level was used for all statistical tests.

Fensulfothion–Montmorillonite Adsorption Systems

The regression equation that gave the best fit of the experimental adsorption data across all treatments of both the Na– and Ca–montmorillonite systems (see R^2 values, Fig. 1 and 2) was

$$\ln Y = b_0 + b_1 \ln X + b_2 X \quad (1)$$

where b_0 , b_1 , and b_2 are regression coefficients to be estimated.

Taking the anti-Ln of equation 1

$$Y = \text{anti-Ln } b_0 \cdot X^{b_1} \cdot e^{b_2 X} \quad (2)$$

$$\text{Let } a = \text{anti-Ln } b_0 \quad (3)$$

$$b = b_1 \quad (4)$$

$$\text{Since } b_2 = \text{constant, hence } e^{b_2} = \text{constant} = d \quad (5)$$

$$\text{or } d = \text{anti-Ln } b_2$$

Substituting equations 3, 4, and 5 into equation 2, the normal form of equation 1 becomes

$$Y = aX^b d^X \quad (6)$$

This regression equation was previously used by Freese (1964). Having shown that this regression equation accurately represented the experimental isotherms, F tests showed that significant differences existed among the four treatments (5% level). Further statistical tests made comparing two treatments at a time indicated that each treatment was significantly different from the other three. The decreasing order of fensulfothion adsorption on the two montmorillonites as affected by the preparation treatment was: Na–montmorillonite: freeze-dried, resuspended > freeze-dried > suspension > freeze-dried, 100% RH. Ca–montmorillonite: freeze-dried > freeze-dried, 100% RH > freeze-dried, re-suspended > suspension.

Fensulfothion–Illite Adsorption Systems

It was difficult to find an equation that was a good fit for all treatments, especially for values of $X(C_e)$ greater than 400. Therefore to make comparisons, the largest X value used was 311 (Ca–illite, treatment 4). For both clays, the isotherms were essentially linear over this reduced range. However,

the \ln transformation was used because the R^2 values were somewhat higher and also because the \ln transformation should stabilize the variance. The best general equation for the illite clays was

$$\ln Y = b_0 + b_1 \ln X \quad (7)$$

where the symbols have the same definition as in equation 1. This implies the relationship

$$Y = aX^b \quad (8)$$

which is in the form of the Freundlich equation

$$X/m = K C_e \quad (9)$$

where $a = K$, $b = 1/n$

The high R^2 values for the Na—illite treatments ($R^2 > 0.9711$, Fig. 3) and for the Ca—illite treatments ($R^2 > 0.969$, Fig. 4) indicate a good fit of the regression equations to the experimental data. The F tests for slope and position of the isotherms showed that there were no significant differences among the Na—illite treatments and that a single regression equation could represent the four treatments ($Y = 0.023 X^{1.31}$ for $X < 311$). All treatments in the Ca—illite system were significantly different except for treatment 3 (freeze-dried, 100% RH) and treatment 4 (suspension). For the Ca—illite system, the decreasing order of fensulfothion adsorption was: freeze-dried > freeze-dried, resuspended > freeze-dried, 100% RH = suspension.

DISCUSSION

The addition of fensulfothion solution to freeze-dried clay (treatment 1) produced greater adsorption than when added to the same clay initially in suspension (treatment 4), except for Na—illite. The presence of water vapor (treatment 3) on the freeze-dried clay reduced fensulfothion adsorption relative to the freeze-dried clay. The effect of resuspending the freeze-dried clay (treatment 2) varied with the saturating cation and the clay, but in all cases (except Na—illite) it exhibited greater adsorption capacities than did the original suspension.

The adsorption behavior of fensulfothion on montmorillonite, discussed previously (Bowman 1973), exhibited strong similarities to alcohol adsorption on clay (German and Harding 1969), and bovine serum albumin (MacRitchie 1972) adsorption on hydrophobic silica. The nature of the albumin adsorption was ascribed to interfacial coagulation, analogous to capillary condensation in gas adsorption. If fensulfothion adsorption on clay occurred via a similar mechanism, factors affecting the surface structure of the clay particles would determine the adsorption pattern. In the present study, such factors included the exchangeable cation, adsorbed water and the effect of the freeze-drying process. The exchangeable cation participated in the adsorption process in two possible ways: (a) by determining the swelling behavior and flocculation state of the clay, and (b) by directly interacting with the fensulfothion molecules (Bowman 1973). The nature of the exterior surface of the montmorillonite clay was very important in fensulfothion adsorption since there appeared to be no interlayer penetration. The greater fensulfothion adsorption by montmorillonite relative to illite was, in part, attributable to the smaller particle size of the montmorillonite ($< 2\mu\text{m}$ vs. 2 to 20 μm for illite). This difference in particle size may have assumed even greater significance since the proposed adsorption mechanism (interfacial coagulation) is quite sensitive to the surface topography of the clay. Changes in particle size, in addition to affecting adsorption capacity, would probably affect the shape of the isotherm, since coalescence or coagulation in the partially completed layers would commence at different solute concentrations in different particle size matrices.

The increased adsorption by freeze-dried clay relative to the same clay in suspension may be attributable to several factors. Upon introduction of the fensulfothion solution to the freeze-dried clay, a rapid mass transport of fensulfothion molecules may have accompanied the wetting front throughout the porous macrostructure (excluding interlamellar spaces). This process would provide the maximum

amount of surface available for fensulfothion adsorption. In contrast, when fensulfothion solution was added to the clay suspension, some smaller pores in the clay flocs may have been rendered inaccessible for adsorption as a result of swelling, or blocking by "thick" water films. The freeze-drying process itself probably altered the adsorption process because of structural alterations in the surface. Both Ahlrichs and White (1962) and Greene-Kelly (1973) reported that the initial freezing process and the following drying process altered the clay structure. Microscopic observations (Ahlrichs and White 1962) indicated a fibrous nature of the gel in edge view and attributed this to the developmental pattern of ice lenses.

The presence of several molecular water layers on the freeze-dried clay (treatment 3) prior to the addition of the fensulfothion solution reduced subsequent fensulfothion adsorption, relative to the freeze-dried clay alone (treatment 1). The water vapor probably initiated the swelling process in the clay thereby modifying the pore sizes and shapes, sealing off some small pores to entry of fensulfothion molecules and in general altering the surface topography of the clay. In addition, the presence of pre-adsorbed water would reduce the effectiveness of the mass transport mechanism in rapidly distributing fensulfothion molecules throughout the pore system of the clay after introduction of the fensulfothion solution.

The effect of the resuspended freeze-dried clay (treatment 2) upon fensulfothion adsorption seemed to be a function of the clay system. With Na–montmorillonite, this treatment produced maximum adsorption, in the Ca–illite system it ranked below the freeze-dried, 100% RH treatment, and in the Ca–montmorillonite system, it ranked third, below the freeze-dried and freeze-dried, 100% RH treatments. However, in all systems (except Na–illite), the resuspended freeze-dried clay produced greater adsorption than the original suspension, leading to the conclusion that the freeze-drying process altered the adsorbing surfaces of the clay. Ahlrichs and White (1962) noted that freeze-dried bentonite shrank very little during the sublimation process and appeared fibrous. Perhaps the freeze-drying process tended to periodically disrupt the stacking of the bentonite sheets, resulting in smaller stacks, a finer particle size and an increased surface area for adsorption. Freeze-drying might also have caused a fraying of the edges of the stacks, accounting for the fibrous nature of the gel in edge view, as noted by Ahlrichs and White (1962). Surface area studies of these clays are warranted to establish whether freeze-drying alters the adsorption of N₂ or ethylene glycol.

INTERPRETATION

Both the freeze-drying process and the conditioning of a dry clay surface with water vapor prior to initiating the adsorption process altered the adsorption of fensulfothion by Na– and Ca–montmorillonite, by Ca–illite, but not by Na–illite. The freeze-drying process increased fensulfothion adsorption relative to the same clay in suspension, whereas preadsorbed water on freeze-dried clay tended to decrease adsorption.

It is not presently known whether variation in adsorbent preparation techniques significantly affect the adsorption of other pesticides, but one should be aware of the possibilities when conducting adsorption studies. (Such drastic changes in moisture content would never occur under natural field conditions.) Although the freeze-drying technique for preparing clays for adsorption studies offers some advantages from the standpoint of clay stability and ease of handling, it does irreversibly alter the surface properties of the clay, as demonstrated by the increased adsorption capacity of the resuspended freeze-dried clay. Since illite is the predominant clay mineral in many Canadian soils, it is suggested that for adsorption studies, the clay might be Na-saturated to minimize the effects of pretreatment upon the adsorption process.

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