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Adsorptive Behavior of Acetochlor on Organoclay Complexes

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Acetochlor [2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl) acetamide] is a selective pre-emergence herbicide used to control broadleaf weeds and annual grasses in corn. It was registered for use in the United States in March 1994 to replace the widely used corn herbicides alachlor, atrazine, butylate, EPTC, 2,4-D and metolachlor (USEPA 1994). Acetochlor is moderately persistent in the environment and is moderately to very mobile in soil. As a result, acetochlor residues are very likely to reach the groundwater and surface water (USEPA 1994), its potential for contamination of groundwater is comparable with those of alachlor and metolachlor (Balinova 1997).

Adsorption on soil is one of the important factors for controlling pesticide movement toward groundwater (Koskinen and Harper 1990). Liu et al. (2001) determined the adsorption of chloroacetanilide herbicides on soils and indicated that the structural differences of pesticides in the same class may be used as a probe to obtain a better understanding to sorption mechanisms of pesticides on soil. Konda et al. (2002) quantified pesticides in liquid phase from batch sorption experiment using high performance liquid chromatography.

The adsorptive behavior under different salinity levels has not been reported. The paper investigates: 1) the adsorptive behavior of acetochlor on different organoclay complexes, 2) the effect of different salinity levels on the adsorption behavior of acetochlor and 3) the effect of phosphonium cations on the adsorption process.

MATERIALS AND METHODS.

The clay used was sodium montmorillonite (SWy-2) obtained from the Source Clays Repository, Clay Minerals Society, Columbia, MO. HPLC- grade methanol, phenyltrimethylammonium (PTMA), hexadecyltrimethylammonium (HDTMA), tetraphenylphosphonium (TPP), methyltriphenylphosphonium (MTPP), tetrabutylphosphonium (TBP), tetraheptylammonium (THA) were purchased as chloride salts from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO, USA; Aldrich Chemical Co., Milwaukee, WI, USA).

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Rice Bran (RB), a bio-adsorbent contains 18 % fat, was purchased from a local market at East Lansing, Michigan, USA. The chemical structure of the organic compounds are shown in Figure 1. Analytical grade of sodium chloride (NaCl) was obtained from Frutarom Laboratory Chemicals (USA). Analytical grade acetochlor, purity 98% was purchased from ChemService USA.

The organoclays were prepared by addition of dry crystals of organic cation equivalent to 0.5 mmol/g clay or 3 times above the cation exchange capacity (0.8 mmol/g) to a 1% (w/v) aqueous suspension of SWy-2 under continuous stirring up to 3 days. The yielded organoclay complex was separated after 30-min centrifugation (6000 *g*), washed three times with distilled water, freeze-dried, ground to < 50μm and kept in plastic bottles at room temperature.

Adsorption of acetochlor on SWy-2 exchanged with a quaternary ammonium or phosphonium organic cation was measured at 25 ± 1 °C. Acetochlor was added at 120 mg /g clay complex having a loading of 0.5 or 0.8 mmol /g clay. Adsorption isotherms on Clay-PTMA0.5, Clay-HDTMA0.5 were determined and simulated by Freundlich equation. To measure the adsorbed amounts, appropriate aliquots of an aqueous solution of acetochlor were diluted by distilled water in 25 ml and were added to 0.025 g organoclay in a 30 ml centrifuge tube. The final concentration of the organoclay was 0.2 g/l. The samples were kept under continuous rotary shaking for 48 hours. The supernatant was separated by centrifugation at 6,000*g* for 1h, and acetochlor was determined by HPLC.

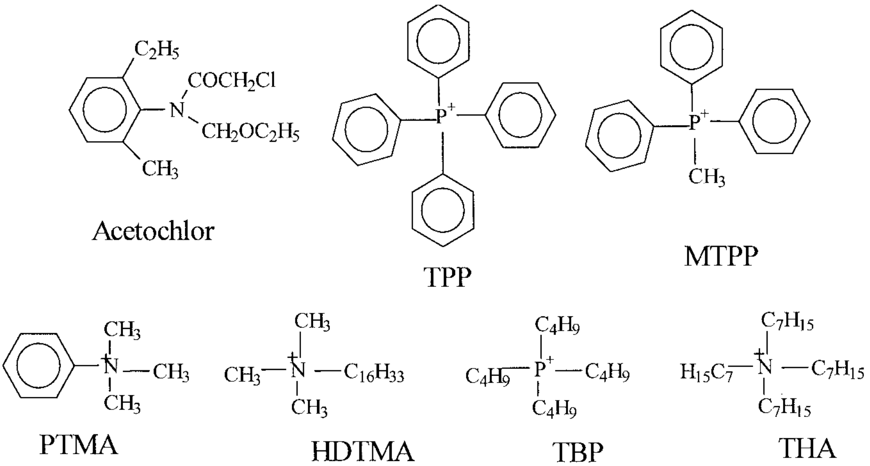

Figure 1. Chemical structures of the organic compounds used.

Effect of salinity on the adsorption behavior of acetochlor was measured on Clay-PTMA0.5 and SWy-2. Adsorption was measured at 0.0, 10, 40, 80, and 150g NaCl/L. In this procedure: appropriate aliquots of an aqueous solution of acetochlor (28.8 mg/l) were diluted in 25 ml distilled water and were added to 0.025 g clay-PTMA0.5 in a 30 ml centrifuge tube containing an appropriate amount of NaCl. The final concentration of the organoclay was 1 g/L. The samples were vortexed for 3 min and kept under continuous rotary shacking for 48 hours at 25 ± 1 °C. The supernatant was separated by centrifugation at 6,000*g* for 1 h, and acetochlor was determined by HPLC.

After modification of Liu et al. (2000) acetochlor concentrations were determined by HP 1090 HPLC (Hewlett-Packard, Wilmington, DE) equipped with an auto-injection system and diode-array detector (DAD). The column was a 250 mm X 4.6 mm (i.d.), reverse-phase Adsorbophore HS C18 (5μm, Alltech, Deefield, IL), injection volume was 25 μl and wave length of the detection was 230 nm, mobile phase was water: methanol 25:75. The flow rate maintained at 1.0 ml min^{-1}. External calibration was used for quantification of acetochlor.

Adsorption data were fit to Freundlich model, $\log C_s = 1/n \log C_e + \log K$, where C_s is acetochlor adsorbed (mg/g), C_e is the equilibrium concentration (mg/l), 1/n and K are physical constants. The slope of the isotherms were normalized to the fraction of organic carbon on the organoclay complexes to produce K_{oc} to compare it with the K_{ow} of acetochlor to understand the mechanism of adsorption. Means of adsorption data were compared by ANOVA.The free energy of the adsorption was calculated by equation (1) (Calvet 1989),

$$\Delta G = -RT \ln K_{oc} \quad (1)$$

where ΔG is the free energy change (K cal mol^{-1}), R is the gas constant (1.986 cal K^{-1} mol^{-1}), T is the absolute temperature.

RESULTS AND DISCUSSION

A linear relation ship was observed between peak area of HPLC chromatogram and acetochlor concentration (data not show). Regression analysis showed a correlation coefficient (R^2) of 0.999 indicating a strong positive dependence. This indicates validity and suitability of the used method and allows for direct measurement of acetochlor in the supernatants.

Adsorption of acetochlor on SWy-2, or organoclays is shown in Figure 2. Little acetochlor was adsorbed on SWy-2 or Arizona clay (SAz1), whereas adsorption on Clay-PTMA0.5 resulted in a dramatic increase in the adsorbed amount of acetochlor among all cases. These results suggest that the Clay-PTMA0.5 has suitable adsorption sites for acetochlor, probably due to similarity in the chemical structure as observed for alachlor, which is a structural analog of acetochlor (El-Nahhal et al. 2000). The low adsorption of acetochlor on SWy-2 is due to the hydrated mineral surface and the hydrophobic nature of acetochlor molecules K_{ow} =1082, (USDA-ARS, Pesticide Property Database 1998). In contrast, Clay-TPP increased the adsorbed amount of acetochlor above that obtained at SWy-2 or bio-adsorbent (RB). Out of that Clay-PTMA, loading the clay with quaternary phosphonium cation competitively improved the adsorbed amount of acetochlor relatively similar to that obtained by using quaternary ammonium organic cation

(BTMA, BTEA) to modify the clay (El-Nahhal et al. 2001). However, the geometry and /or the molecular size of phosphoinium cation may not optimize interaction between the anilidic group (C-N) of acetochlor and phosphonium (C-P). The highest adsorbed amount of acetochlor was observed on a partially hydrophobic clay exchanged with a smaller aromatic cation (PTMA). The larger phosphonium aromatic cations (MTPP, TPP) have 3-4 phenyl rings, a larger bond length (C-P). These two parameters apparently reduce the strength of the interaction between acetochlor and the adsorbed organic cation.

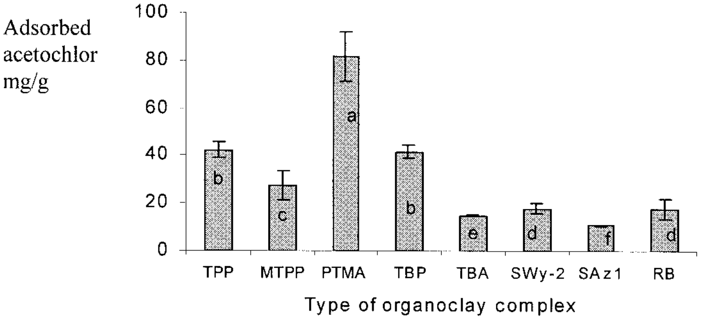

Figure 2. Adsorption of acetochlor on different organoclays. Bars indicate standard deviation. Columns have the same letter are not significantly different at p =0.05 level of significance.

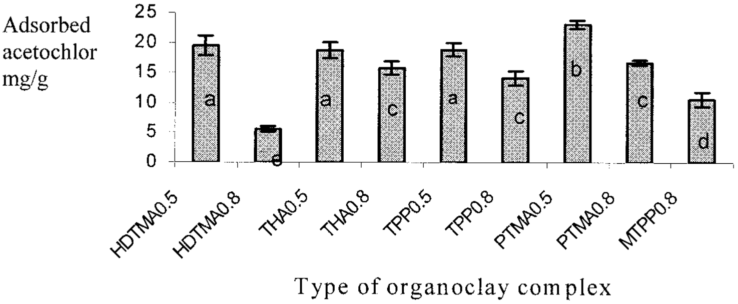

Figure 3. Adsorption of acetochlor on organoclays with varied loadings. Bars indicate standard deviation. Acetochlor was added at 28.8 mg/g clay complex. Columns have the same letter are not significantly different at p =0.05 level of significance.

Adsorption of acetochlor on organoclays having varied loadings (0.5/ 0.8 mmol/g clay) is shown in Figure 3. It is evident that partial saturation (0.5 mmol/g) with organic cation resulted in significantly larger adsorbed amount of acetochlor than obtained at relatively full hydrophobic clay (0.8 mmol/g).These data provide additional evidence of physical adsorption rather than portioning and indicate that the fraction of organic carbon is not the key issue in the adsorption process. It seems that the chemical structure of both the organic cation and the herbicide have a strong influence on the adsorption process. These data agree with Liu et al. (2001), who reported the effect of structural in the sorption mechanisms on soil. However, partial loading (0.5 mmol/g clay) seems to optimize the adsorption of acetochlor, probably due to a better geometrical fit as discussed before for other cases (El Nahhal et al. 2000). The data reveal that relatively full hydrophobic surfaces, does not necessarily imply optimal interactions between the herbicide molecules and the organoclay. Partially hydrophobic clay (0.5mmol/g) is the best among all cases.

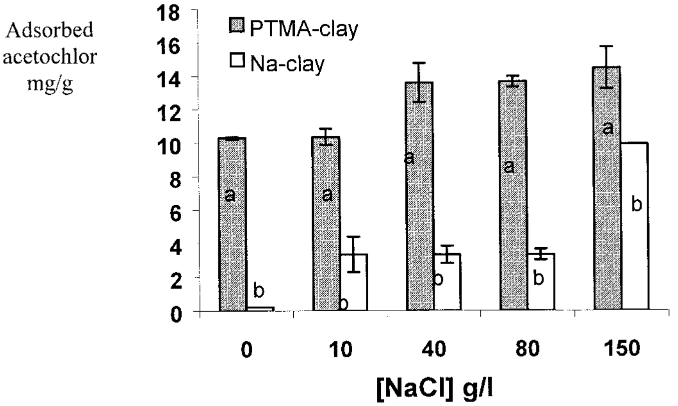

Figure 4. Adsorption of acetochlor on Clay-PTMA0.5 or Swy-2 (Na-Clay) at various NaCl concentration. Bars indicate standard deviation. Columns have the same letter are not significantly different at *p* =0.05 level of significance.

Adsorption of acetochlor under various NaCl concentrations is shown in Figure 4. It can be seen that adsorption of acetochlor on SWy-2 or Clay-PTMA0.5 increased almost linearly as the NaCl concentration increased in the equilibrium solution, indicating a strong positive dependence. The explanation of these results is that addition of salt may produce ion during the dissolution of a salt that tightly bind water into hydration shells, which has long been recognized to reduce the volume of aqueous solution even macroscopically by a process known as electrostriction. These tightly bound water molecules are unavailable to dissolve into. Consequently, as more and more NaCl added to the aqueous solution less and less water remains to create a cavity in which to accommodate acetochlor. This reduction in the aqueous solubility of a compound has been shown to increase adsorption. Recently, El-Nahhal (2002) demonstrated similar effect on the adsorption of chlorpyrifos under various NaCl concentrations. However, effect of salt in the adsorption tends to be similar to the effect of partitioning of non-ionic compound into two phases one of them being water. Regression analysis of a logarithmic scale of the data in Figure 4 gave equation (2), with a value of R^2 equal to 0.9963, where Y represent the log scale of the adsorbed amount (mg/g) and X represent the log scale of NaCl concentration (mg/l).

$$Y= 0.1260X+ 0.5103 \qquad (2)$$

These data indicate strong and positive associations between adsorption and concentration of NaCl. Effect of NaCl concentrations of the free energy of the adsorption reaction on Clay-PTMA calculated from eq (3), (Kishk et al 1979) are shown below, where C_i is the initial concentration of acetochlor.

$$\Delta G=-RT\ln (Ci/Ce) \quad (3)$$

The calculated values of ΔG are $-0.7862\pm(0.006)$ and $-1.8131\pm(0.052)$ K cal mol^{-1} for the adsorption from distilled water and hyper-saline solution (150 g/l). These values are always negative quantity, and indicated that acetochlor adsorbed on the surface of organoclay or the organoclay has undergone an expansion to accommodate acetochlor molecules. Moreover, the values of ΔG are decreased proportionally as the concentration of NaCl increased. This findings indicate that the adsorption reaction is a spontaneous and can further be enhanced by the addition of salt.

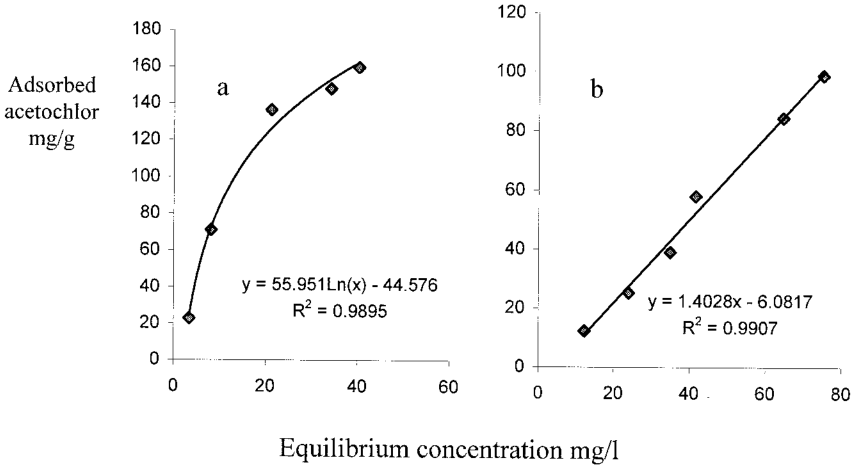

Figure 5. Adsorption isotherms of acetochlor on montmorillonite exchanged with PTMA at a loading of 0.5 (a) or with HDTMA0.5 (b).

Figure 5 presents the adsorption isotherms of acetochlor on Clay-HDTMA0.5 and Caly-PTMA0.5. It is obvious that the adsorbed amount of acetochlor on Clay-PTMA0.5 followed a logarithmic relationship with a correlation coefficient (R^2)value of 0.9895. These data indicate a high affinity of acetochlor to be adsorbed on Clay-PTMA0.5. A linear relationship was observed with the Clay-HDTMA0.5. The value of R^2 equal to 0.99 indicating a good interaction. The Freundlich coefficient K_d value normalized to the fraction of organic carbon gave values of K_{oc} , 6382 and 1381 for the adsorption on Clay-PTMA0.5 and Clay-HDTMA0.5 respectively. K_{oc} value for Clay-PTMA0.5 is higher than the K_{ow}

value (1082), indicating that adsorption occur via physical interaction probably via C=O or C-N and/or through π-π interactions of phenyl rings. The pretty close value of K_{oc} for Clay-HDTMA0.5 to that of K_{ow} suggests that acetochlor interaction occur via partitioning. Thus acetochlor sorption on partially hydrophobic clay is not primarily due to partitioning. It is dependent on the saturation state of the clay surfaces, size and shape of the organic cations exchanged on the clay.

The calculated ΔG^o value using eq (1) showed that the value obtained at Clay-PTMA0.5 (-5.18 K cal mol^{-1}) is significantly higher than the value obtained by using Clay-HDTMA0.5 (-4.28 K cal mol^{-1}). This indicates the different affinity of interaction. Moreover, the pretty closed value of Clay-HDTMA0.5 and the corresponding one obtained using K_{ow} value (–4.13 K cal mol^{-1}) provide an evidence of similar mode of interaction which assumed to be partitioning of acetochlor on Clay-HDTMA0.5. These data are in accord with K_{oc} values as elaborated above. This indicates that acetochlor might be adsorbed on Clay-PTMA0.5 by physical means and on Clay-HDTMA0.5 by partitioning as elaborated previously for other cases (Boyd et al. 1988). However, it should be born in mind that other factors, such as the variation in surface area of the organoclays, the active groups, degree of hydrophobicility, surface acidity or basicity of the organoclay complex affect the adsorption of acetochlor. The relatively higher adsorption capacity of acetochlor on Clay-PTMA0.5 indicate that acetochlor could interact through the active groups with the organoclay complex, or it may penetrate through the channels of the organoclay.

The environmental relevance of this work emerges from the fact that organoclay complexes have been shown: to clean water (Boyd et al. 1988); to reduce volatilization and photodegradation (El-Nahhal et al. 1999); to reduce leaching and improved herbicidal activity (El-Nahhal et al. 2000); and rrecently to enhance biodegradation of petroleum model compounds by cyanobacterial mats (Abed et al. 2002). These findings may provide better methods for preparation of pesticide formulations for the use in different environments.

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