DIVISION S-2—NOTES

INTERACTIONS OF ACIDIC HERBICIDES BENTAZON AND DICAMBA WITH ORGANOCLAYS

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Abstract

We determined the sorption mechanism of the acidic herbicides bentazon [3-(1-methylethyl)-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2-dioxide] and dicamba (3,6-dichloro-2-methoxybenzoic acid) on two organoclays, octadecylammonium (ODA)- and hexadecyltrimethylammonium (HDTMA)-exchanged Arizona montmorillonite (SAz-1), as part of a study to determine their potential use as sorbent materials for ionizable organic pollutants. To determine the mechanisms involved in the sorption process, herbicide-organoclay complexes were characterized by x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). In general, the d_{001} values of SAz-HDTMA and SAz-ODA organoclays expanded after herbicide saturation, indicating interlayer sorption of the herbicide. Also, FTIR spectroscopic studies suggested weak hydrophobic interactions between these herbicides and the interlayer organic phase of the organoclays. However, H bonding between these herbicides and the monosubstituted amino group in SAz-ODA reinforced the strength of the hydrophobic interactions resulting in nonreadily reversible sorption on that organoclay. These results suggest that organoclays can be used to remove this type of pollutants from water or soils.

ORGANOCLAYS HAVE BEEN SHOWN to be good sorbents in removing hydrophobic organic chemicals and polar pesticides from water (Boyd et al., 1988; Lee et al., 1989; Hermosin and Cornejo, 1992, 1993; Hermosin et al., 1995; Zhao et al., 1996; Pantani et al., 1997; Xu et al., 1997; Celis et al., 1999). Hydrophobic and polar interactions between the pesticide and the alkyl chains of the OCl and mineral surfaces, respectively, can reduce pesticide mobility in soil. Recent studies further suggest that OCl can be advantageously used to restore soil and water contaminated with polar herbicides (Socias-Viciana et al., 1998; Aguer et al., 2000; Carrizosa et al., 2000, 2001). Before organoclays can be used in protection and restoration of soils and waters contaminated with organic pollutants, information is needed on specific sorbent-pesticide interactions, including information on desorption (Hermosin and Cornejo, 1992, 1993; Celis et al., 1999).

Previous research has reported information about the sorption behavior of several organoclays for the acidic

herbicides such as bentazon, dicamba, imazamox, and picloram and their potential use as immobilizing agents in contaminated soils (Carrizosa et al., 2000, 2001; Celis et al., 1999, 2002). Hydrophobic interactions with polar contributions were suggested to be responsible for sorption of both herbicides on organoclays, with the magnitude of sorption dependent on the nature of the saturating alkylammonium cation. The objective of this study was to determine the possible mechanisms involved in the sorption of bentazon and dicamba on ODA and HDTMA-exchanged montmorillonite by XRD and FTIR.

Materials and Methods

Bentazon (97% pure) is a crystalline solid with a solubility of 570 mg L⁻¹ water (2.08 mM) (20°C) and pK_a 2.3 (Worthing and Hance, 1991). Bentazon was kindly supplied by BASF (Research Triangle Park, NC). Dicamba (99% pure) is a crystalline solid with a solubility of 6.5 g L⁻¹ water (29.4 mM) (25°C), and pK_a 1.95 (Worthing and Hance, 1991). Pure analytical dicamba was purchased from Chem Service (West Chester, PA).

Arizona montmorillonite (SAz-1), supplied by the Clay Mineral Repository of the Clay Minerals Society (Aurora, CO), was used as received in the preparation of the organoclays. SAz1 was Ca saturated and has a cation exchange capacity (CEC) of 120 cmol kg⁻¹ (Van Olphen and Fripiat, 1979). The organoclays were prepared as previously described (Carrizosa et al., 2000, 2001). In brief, 100 g of the mineral clay was treated with an ethanol/water (50:50) solution of the quaternary (HDTMA) or primary (ODA) alkylammonium chloride/bromide containing an amount of cation equivalent to 100% of the sample CEC. The suspensions were shaken, centrifuged, washed with aqueous ethanol followed by deionized (DI) water until halide free, and then freeze dried. The physicochemical properties of the organoclays are shown in Table 1.

Herbicide saturated organoclays were prepared by five successive treatments of 20 mg of the organoclays with 8 mL of a concentrated solution of the herbicides in DI water. The amount of herbicide sorbed after successive treatments of organoclays with the herbicide solutions was calculated from the sum of the decreases in herbicide solution concentrations after each successive treatment. The basal spacings of the organoclays-herbicide complexes were measured by x-ray in a Siemens D-5000 equipment (Siemens/Brukerans, Karlsruhe Germany) with CuK α radiation on an oriented film supported on a glass-slide and a goniometer rate of 2° min⁻¹. This film was prepared by depositing aliquots of approximately 2% methanol/water (50:50) suspensions. The samples were also analyzed by FTIR spectroscopy (Nicolet PC spectrometer, Nicolet Instruments Corp., Madison, WI) on KBr disks.

Results and Discussion

At low solution concentrations, high sorption affinities of the acidic herbicides bentazon, dicamba, and picloram were previously found for SAz-1 saturated

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Abbreviations: CEC, cation-exchange capacity; FTIR, Fourier transform infrared; HDTMA, hexadecyltrimethylammonium; ODA, octadecylammonium; XRD, x-ray diffraction.

Table 1. Physicochemical properties and Freundlich constants of organoclays.[†]

Sorbent	CEC [†]	%OC	%OCtS	d ₀₀₁	Bentazon [‡]		Dicamba [§]		Picloram	
					K _f	1/n _f	K _f	1/n _f	K _f	1/n _f
				nm						
SAz-HDTMA	120	22.8	85	2.4	826	0.41	272	0.50	240	0.48
SAz-ODA	120	25.5	98	3.2	285	2.7	352	2.1	504	1.7

[†] CEC, cation exchange capacity; %OC, % organic C content; %OCtS, % organic cation saturation; d₀₀₁, basal spacing.

[‡] Data from Carrizosa et al. (2000).

[§] Data from Carrizosa et al. (2001).

^{||} Data from Celis et al. (2002).

with a large quaternary organic cation (HDTMA), while low sorption affinities were found for this clay saturated with a primary alkylammonium cation (ODA) (Carrizosa et al., 2000, 2001; Celis et al., 2002). It was suggested that hydrophobic interactions driving the sorption between herbicide molecules and organoclay would be predominant in the case of SAz-HDTMA, whereas polar herbicide-solvent interactions would predominate for SAz-ODA. This was supported by the slopes of the Freundlich sorption isotherms, where $1/n_f \ll 1.0$ for SAz-HDTMA and $1/n_f \gg 1.0$ for SAz-ODA. Desorption isotherms for dicamba (Carrizosa et al., 2001), picloram (Celis et al., 2002), and bentazon (unpublished results) with SAz-HDTMA exhibited reversible sorption for the three herbicides, whereas there was hysteresis during desorption from SAz-ODA. Because of these differences in strengths of herbicide-organoclay interactions, these two organoclays were selected for the mechanistic studies.

The amounts of acidic herbicides sorbed after successive treatments of SAz-HDTMA and SAz-ODA with herbicide solutions, show the high sorption capacity of the organoclays for bentazon and dicamba (Table 2). In previous research, greater sorption was reported on SAz-HDTMA as compared with SAz-ODA (Carrizosa et al., 2000, 2001). The d₀₀₁ values (Table 2) indicate that herbicide-organoclay complexes expanded upon sorption of the herbicide. SAz-HDTMA, after saturation with the herbicides, had the largest d₀₀₁ expansion, increasing from 2.4 to 3.8 nm, and 3.7 nm for bentazon and dicamba, respectively, whereas SAz-ODA only increased from 3.2 to 3.5 nm and 3.6 nm, respectively. The different sorption capacities for these herbicides and the resulting basal spacing expansion can be related to the initial interlayer arrangement of the alkylammonium cation in these clays, and the molecular size of the corresponding herbicide. In general, basal spacing expansion as a result of the herbicide exposure confirms the interlayer sorption of the two herbicides in both organoclays.

Table 2. Amount of herbicide sorbed and basal spacings (d₀₀₁) values of the OCI-herbicide complexes.

Organoclay	Bentazon		Dicamba	
	Bentazon sorbed	d ₀₀₁	Dicamba sorbed	d ₀₀₁
	mmol kg ⁻¹	nm	mmol kg ⁻¹	nm
SAz-HDTMA	960	3.8	856	3.7
SAz-ODA	666	3.5	775	3.6

Fig. 1. Fourier transform infrared spectra of: bentazon (a), SAz-HDTMA (b), SAz-HDTMA + bentazon (c), SAz-ODA (d), and SAz-ODA + bentazon (e).

Fourier transfer infrared spectra of pure herbicides, organoclays and organoclay-herbicide complexes are shown in Fig. 1 and 2. The FTIR band assignments in the following text are in accordance with Bellamy (1980). Figures 1 and 2 show that some of the bands occurred at the same frequency as in pure compound, while other bands were slightly shifted and some new bands appeared. For instance, organoclay spectra in Fig. 1b and d, and 2b and d, show differences in the OH and NH regions. SAz-HDTMA (Fig. 1b and 2b) shows bands at 3426 and 1640 cm⁻¹ (ν_{OH} and δ_{OH}) corresponding to molecular water that does not appear in SAz-ODA (Fig. 1d and 2d). SAz-ODA has bands at 3437 and 1636 cm⁻¹ corresponding to the free NH groups of the primary alkylammonium (a little amount of molecular water can be included in these frequencies), in addition to weak bands at 3247 and 1610 cm⁻¹ arising from NH bonded to basal oxygen atoms of the layer. Although the organic clays were washed with aqueous ethanol to remove all octadecylamine, washing may have been incomplete and there is a possibility that SAz-ODA may have contained both octadecylammonium and octadecylamine.

The differences in organoclays are related to the structure and saturation level of the alkylammonium cations. The long linear chain of the primary alkylammonium resulted in a more compact packing of those cations in the interlayer, creating a highly hydrophobic organic layer, which can prevent water intake. In contrast, the asymmetric structure of the quaternary alkylammonium, as well as its lower saturation level, leaves some polar room between the groups that can be occu-

Fig. 2. Fourier transform infrared spectra of: dicamba (a), SAz-HDTMA (b), SAz-HDTMA + dicamba (c), SAz-ODA (d), and SAz-ODA + dicamba (e).

pied by water molecules, probably associated with basal oxygens of the clay network or to residual inorganic cations.

The main feature of bentazon-SAz-HDTMA (Fig. 1c) complex is the near absence of bands 3426 and 1640 cm^{-1} , indicating the displacement of the initial water molecules by bentazon. It appears bentazon is retained in monomeric form, as deduced from dissipation of the strong band of bonded NH at 3124 cm^{-1} and the shifting of the $\nu_{\text{C=O}}$ from 1656 cm^{-1} to higher frequency, 1685 cm^{-1} , which indicates the rupture of the intermolecular bond (bentazon-NH-O=C-bentazon) between bentazon molecules in the pure compound. The small band at 3431 cm^{-1} suggests a weak polar interaction between bentazon NH with the basal oxygen atoms substituting the water molecules released. The retention of bentazon by SAz-HDTMA can be mainly attributed to the hydrophobic interaction between the bulky herbicide molecule and the alkylchains of the quaternary cation. This mechanism supports the reversibility observed in the sorption-desorption isotherms. These results are very similar to those reported by Celis et al. (2002) for the sorption of picloram on SAz-HDTMA, in which case additional interactions between the -NH_2 group of the herbicide and the clay surface were involved.

In the case of bentazon-SAz-ODA complexes (Fig. 1e), the increase in the intensities of bands at 3247 and 3180 cm^{-1} suggest the implication of the NH groups of the OCl in H bonding. This is supported because the initial $\nu_{\text{C=O}}$ bond of bentazon at 1656 cm^{-1} (Fig. 1a) splits into two bands in the bentazon-SAz-ODA complex (Fig. 1e) at 1672 and 1593 cm^{-1} . The 1593 cm^{-1}

band would correspond to $\nu_{\text{C=O}}$ strongly bonded through H bond to the NH group of the alkylammonium. The band at 1672 cm^{-1} implies the existence of some monomeric species retained in the paraffinic layer of the primary alkylammonium by weak hydrophobic interactions. Therefore, in this case two types of interaction are involved, hydrophobic interactions and strong polar H bonds. The strong polar interactions between $\nu_{\text{C=O}}$ of bentazon and the amino group of the alkylammonium would be responsible of the significant hysteresis observed in the sorption-desorption isotherms. Celis et al. (2002), found a similar behavior in sorption of picloram on SAz-ODA, but in that case, interactions between the ionized- COO^- group of picloram and the interlayer primary alkylammonium of the organoclays were suggested.

The FTIR spectra of dicamba interactions with HDTMA and ODA are shown in Fig. 2. The band at 1730 cm^{-1} for dicamba-SAz-HDTMA was assigned to the C=O stretching vibration of the protonated carboxylic group of dicamba and indicates that sorption involved the undissociated form of dicamba. In addition, a shift of $\nu_{\text{C=O}}$ of the carboxylic group from 1711 to 1730 cm^{-1} also suggests the presence of monomeric molecules in an undissociated form (Zhao et al., 1996). This mechanism supports the reversibility observed in the sorption-desorption isotherms.

In the case of ODA, a strong diminution of the free $\nu_{\text{N-H}}$ at 3437 cm^{-1} is observed, together with an increase of the bonded $\nu_{\text{N-H}}$ at 3262 cm^{-1} , suggesting the implication in H bonding. Moreover, the carboxylic $\nu_{\text{C=O}}$ at 1711 cm^{-1} in the pure herbicide practically disappeared, showing that most of dicamba is H bonded to NH group of the interlayer alkylammonium, and the bond is displaced at lower frequencies at 1629 cm^{-1} . It is interesting to point out that a new band appears at 1515 cm^{-1} , which can be assigned to the stretching of C-O in a dissociated carboxylic group. This dissociation of some dicamba molecules can be induced by a strong electrostatic interaction of the anionic form with the positively charged alkylammonium cations. All the FTIR features described above, suggest that in addition to hydrophobic interactions, dicamba is sorbed by strong polar and ionic bonding, which in turn explains the hysteresis observed for the sorption-desorption process.

In summary, the results of this work show that the modification of montmorillonite with alkylammonium cations resulted in interlayered organoclays with high sorptive properties for acidic herbicides. X-ray diffraction and FTIR studies indicate interlayer sorption of bentazon and dicamba in SAz-HDTMA and SAz-ODA and weak interactions between the herbicide molecules and SAz-HDTMA that are in agreement with the high reversibility observed in the sorption-desorption isotherms. For SAz-ODA, H bonding contributed to increase the strength of interaction, which in turn resulted in decreased desorption. Environmental implications for these results suggest that organoclays can be used to remove this type of pollutant from water or soils or as support for the slow release formulation of anionic or acidic acids.

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