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Sorption and Degradation of Azimsulfuron on Iron(III)-Rich Soil Colloids

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The sorption of *N*-[[(4,6-dimethoxypyrimidin-2-yl)amino]carbonyl]-1-methyl-4-(2-methyl-2*H*-tetrazole-5-yl)1*H*-pyrazole-5-sulfonamide (AZS) on an iron oxide, iron(III)−humate, and an Fe^{3+}-saturated clay was studied using a batch equilibrium method. Generally, 20 mg of each colloid was equilibrated with 20 mL of AZS solution (1.5−12.7 μM). The sorption on iron−montmorillonite and iron oxide was rapid, and the equilibrium was attained within 1.5 and 5 h, respectively. In the case of Fe-saturated humic acid the equilibrium time was 20 h. After equilibration, the phases were centrifuged (19000*g*, 15 min) and the supernatant was sampled and analyzed by HPLC. The values of Freundlich constants indicate that iron oxide (K_{ads} = 199.5) shows the highest sorptive capacity toward AZS, followed by iron(III)−clay (K_{ads} = 146.6) and iron(III)−humate (K_{ads} = 108.2). With elapsing time, AZS degradation was observed in all colloidal suspensions. Iron-humate ($t_{1/2}$ = 136 h) is most effective in promoting AZS degradation, followed by iron oxide ($t_{1/2}$ = 204 h) and iron−clay ($t_{1/2}$ = 385 h). The metabolites 2-amino-4,6-dimethoxypyrimidine and 1-methyl-4-(2-methyl-2*H*-tetrazole-5-yl)-1*H*-pyrazole-5-sulfonamide, arising from a hydrolytic cleavage of the sulfonylurea bridge, were the only byproducts observed. A Fourier transform infrared study suggests that the sorption of AZS on iron−clay involves the protonation of one of the two basic pyrimidine nitrogens induced by the acidic water surrounding the saturating Fe^{3+} ions. Instead, the formation of a six-membered chelated complex favors the sorption of AZS on iron oxide.

KEYWORDS: Azimsulfuron; sorption; degradation; iron oxide; iron−clay; iron−humate

INTRODUCTION

Azimsulfuron (AZS, trade name Gulliver, **Figure 1**) is a sulfonylurea herbicide for the postemergence control of *Echinochloa* species, broadleaf and sedge weeds in rice production. This herbicide, like other sulfonylureas, inhibits the activity of the enzyme acetolactate synthase (ALS), which is essential in the biosynthesis of the branched-chain amino acids valine, leucine, and isoleucine (*1*).

Herbicides used in paddy fields during the flooding season can easily cause pollution through runoff into rivers. The sorption from aqueous solution onto solid surfaces is a key process in the transport and distribution of an organic contaminant in the environment (*2*). AZS, being a weak acid (pK_a = 3.6), occurs mainly in dissociated form in agricultural soils; therefore, it could exhibit a significant mobility (*3*).

A recent study performed by us on the AZS retention by soil indicated that the highest level of sorption was measured on soils with low pH and high organic carbon content (*4*). Smectite clay minerals and iron oxides have also been documented to contribute to AZS sorption (*4*). Several studies demonstrated that sorption mechanisms on soil colloids are generally related, besides to the specific properties of the colloid, to the nature of the exchangeable metal ions (*5*−*7*). Iron(III) is a common soil constituent (*8*) that occurs mainly in colloidal iron(III) oxides, but can be associated to humic substances in stable complexes or be an exchangeable cation in soil clay structures. The present work was aimed to study the role of Fe-containing colloidal species in AZS sorption. Therefore, the sorption of AZS was tested on an iron oxide, iron(III)−humate, and an Fe^{3+}-saturated clay mineral. Moreover, because prolonged contact times of AZS aqueous solutions with colloid surfaces promoted the hydrolysis of the herbicide, a study of the AZS degradation kinetics was included.

MATERIALS AND METHODS

Materials. White crystals of AZS (99.7% purity, mp = 170 °C; vapor pressure = 4×10^{-6} mPa) were supplied by DuPont de Nemours France SA (Centre Europeen de Recherches), Nambsheim, France. Its solubility (20 °C) is 72 mg L^{-1} water (pH 5), 1050 mg L^{-1} (pH 7) and 6540 mg L^{-1} (pH 9). AZS purity was checked by high-performance liquid chromatography (HPLC). The AZS byproduct 2-amino-4,6-

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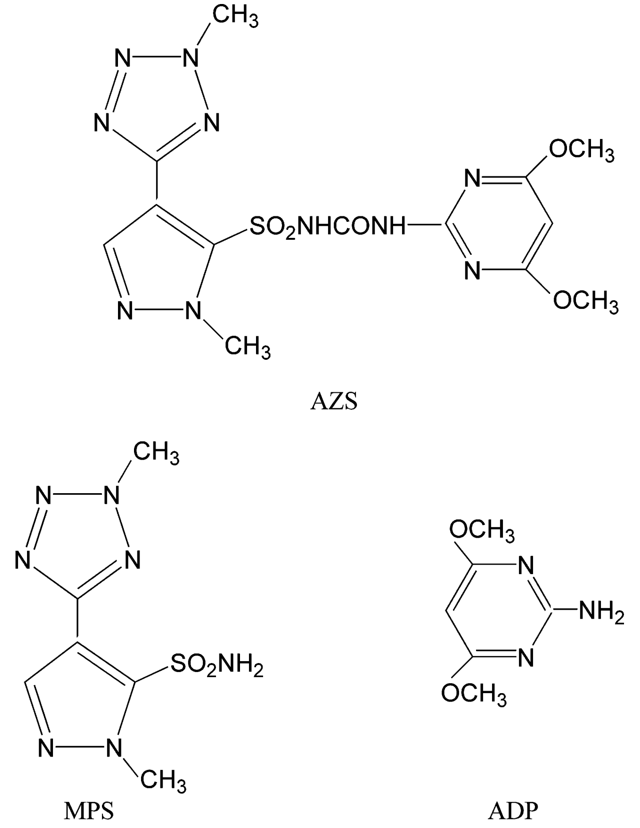

Figure 1. Structures of azimsulfuron and its metabolites 1-methyl-4-(2-methyl-2*H*-tetrazole-5-yl)-1*H*-pyrazole-5-sulfonamide (MPS) and 2-amino-4,6-dimethoxypyrimidine (ADP).

dimethoxypyrimidine (ADP, 98.0% purity) was supplied by Aldrich, Milano, Italy. Azimsulfuron hydrochloride (AZS·HCl) was prepared by bubbling anhydrous HCl into a $CHCl_3$ solution of AZS for 1 h, according to a general procedure for obtaining the hydrochlorides of nitrogenous heterocycles. A white precipitate formed, which was filtered and dried under vacuum. All of the solvents were of HPLC grade (Carlo Erba Reagenti, Milano, Italy) and were used without further purification.

Montmorillonite no. 26 (bentonite) from Crook County, Wyoming, supplied by Ward's Natural Science Establishment, Rochester, NY, was used. The <2-μm fraction was separated by sedimentation in Atterberg cylinders and freed from residual organic matter by treatment with hydrogen peroxide (30%) at 70 °C for 16 h. The cation exchange capacity (CEC) of the sodium form was 90.2 cmol kg^{-1}, as determined according to the method of Hendershot and Duquette (*9*). Fe^{3+}-exchanged montmorillonite was prepared by several treatments of the clay with a 0.1 M solution of $FeCl_3$; then the sample was centrifuged, washed repeatedly with deionized water until Cl^- free, and dried at room temperature.

Hydrated ferric oxide was prepared by adding 0.50 mol of $FeCl_2$ to an equivalent amount of 2 M KOH (250 mL) under rapid stirring (*10*). The precipitate was immediately washed with distilled water and dried under vacuum. It was amorphous according to X-ray analysis and completely soluble in ammonium oxalate (pH 3).

Humic acid was obtained from the soil from Monghidoro (Italy) according to the procedure of Stevenson (*11*). Iron(III)−humate was prepared by several treatments of humic acid with 0.1 M $FeCl_3$. Then the sample was centrifuged, washed repeatedly with deionized water until Cl^- free, dried at room temperature, and finally freeze-dried.

Sorption. AZS sorption isotherms were obtained on different colloidal systems using a batch equilibrium method. In general, duplicate samples of colloid (20 mg) were equilibrated in polyallomer centrifuge tubes with 20 mL of aqueous herbicide solution. The tubes were previously checked to verify that they did not adsorb AZS. The initial concentration of herbicide ranged between 1.5 and 12.7 μM. The tubes were shaken in an end-over-end shaker (70 rpm) at 25 ± 2 °C until equilibrium was reached. Preliminary kinetic batch studies indicated that the equilibrium was reached within 1.5, 5, and 20 h on iron−clay, iron oxide, and iron−humate, respectively. No degradation took place within the aforementioned times. AZS sorption was also studied on humic acid (pH 3.5, equilibrium time = 5 h) and humic acid modified by the addition of $Ca(OH)_2$ (pH 4.6, equilibrium time = 20 h) to compare the sorptive capacity with that of iron−humate. After equilibration, the suspensions were centrifuged at 19000*g* for 15 min and the supernatant was pipetted off and analyzed immediately. The amount adsorbed by the colloid was calculated from the difference between the initial and final concentrations of AZS in solution.

Sorption data were fit to the logarithmic form of the Freundlich equation, $\log C_s = \log K_{ads} + 1/n_{ads} \log C_e$, where C_e (in μmol kg^{-1} units) is the amount of herbicide adsorbed by the colloid, C_e (in μM units) is the equilibrium concentration in solution, and $\log K_{ads}$ and $1/n_{ads}$ are empirical constants representing the intercept and the slope of the isotherm, respectively.

Degradation. AZS degradation experiments were performed in colloidal aqueous suspensions. In general, 50 mg of colloid was suspended in 50 mL of AZS aqueous solution [13.2 μM for iron(III)−montmorillonite and 12.8 μM for iron−humate and iron oxide] in polyallomer centrifuge tubes. A colloid-free blank was carried out in distilled water buffered at pH 4.8. The samples were kept at 25 ± 2 °C under stirring. After equilibrium was reached, kinetic studies were carried out by removing 0.5-mL aliquots at different times. The suspensions were ultracentrifuged, and AZS and its degradation products were analyzed in the supernatant by HPLC. The experiments were run in duplicate. AZS degradation was also followed in the presence of humic acid suspension buffered at pH 4.6 (AZS concentration = 12.4 μM) in the same way as reported above.

Kinetic data were fit to a first-order rate law, $\ln C/C_0 = -k_{obs}t$, where C is the herbicide concentration (in μM units) at the time t (h), C_0 is the initial herbicide concentration, and k_{obs} (in h^{-1} units) is the first-order rate degradation constant.

In all systems investigated, the degradation afforded two byproducts: ADP and 1-methyl-4-(2-methyl-2*H*-tetrazole-5-yl)-1*H*-pyrazole-5-sulfonamide (MPS). MPS was a colorless oil: IR (KBr) ν (cm^{-1}) 3285, 3203, 1601, 1560, 1383, 1355, 1179; ^1H NMR ($CDCl_3$) δ 8.1 (1H, s), 6.75 (2H, m), 4.38 (3H, s), 4.18 (3H, s).

HPLC Analyses. The concentration of AZS and its degradation products was determined by HPLC. The system was assembled as follows: a Waters 1515 pump equipped with a Waters 2487 UV−vis programmable detector operating at 240 nm; Breeze chromatography software; a μBondapak C_{18} analytical column (10 μm, 3.9 × 300 mm). The mobile phase was acetonitrile plus water (50 + 50 by volume, pH 2.7) at a flow rate of 1 mL min^{-1}. The retention times under these chromatographic conditions were 3.4, 3.8, and 6.8 min for ADP, MPS, and AZS, respectively. The quantitative determination of AZS was performed by using an external standard. Calculations were based on the average peak areas of the external standard. The detection limit for AZS was 0.1 mg L^{-1}, namely, the herbicide concentration corresponding to a detector response approximately twice the background signal.

Infrared Analyses. FT-IR spectra were recorded with a Nicolet 205 spectrophotometer over the range of 4000−600 cm^{-1}. The spectra of AZS, AZS·HCl, and iron oxide−AZS complex were recorded on KBr disks. The spectrum of AZS adsorbed on Fe^{3+}-exchanged montmorillonite was recorded on a self-supporting film (*12*), which was prepared by evaporating 5 mL of an aqueous clay suspension (2 g of clay in 100 mL of H_2O) on a polyethylene sheet at room temperature (*13*). The air-dried films were divided into two parts. One piece was placed into a 2% AZS $CHCl_3$ solution for 24 h, then removed, rinsed several times with the pure solvent, and air-dried. The other was treated similarly, but without herbicide. AZS was also adsorbed on iron oxide. A 5-mL aliquot of a 2% AZS $CHCl_3$ solution was added to 10 mg of iron oxide. The suspension was stirred for 24 h, then filtered; the iron oxide−AZS complex was washed several times with pure $CHCl_3$ and air-dried.

The IR spectra of the iron−clay− and iron oxide−AZS complexes were recorded immediately after air-drying. A differential spectrum was obtained for the AZS−montmorillonite complex by subtracting the spectrum of the blank clay film from those of the clay−AZS complex. Only IR absorptions in the range of 2000−1200 cm^{-1} are

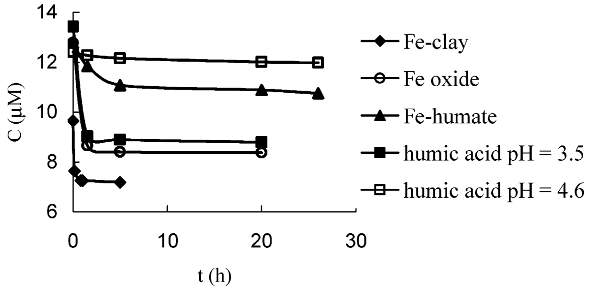

Figure 2. Time dependence of the sorption of azimsulfuron on the sorbents studied.

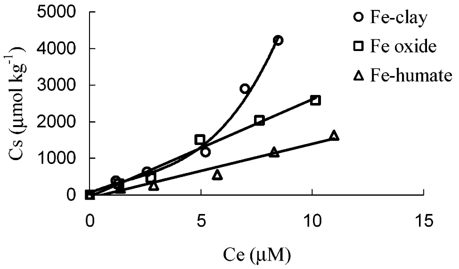

Figure 3. Sorption of azimsulfuron on iron colloids.

Table 1. Freundlich Parameters for the Sorption of Azimsulfuron on Iron Colloids and Humic Acid

system	pH[a]	K_{ads}	$1/n_{ads}$	r[b]
iron oxide	4.8	199.5	1.13	0.980
iron–clay	4.4	146.6	1.43	0.933
iron–humate	4.6	108.2	1.07	0.970
humic acid	3.5	103.0	1.45	0.997
humic acid	4.6	1.8	2.77	0.974

[a] pH of aqueous suspension. [b] Correlation coefficient.

discussed here because this region provides evidence for the sorption mechanisms. All of the spectra were the means of at least 64 scans at 4 cm^{-1} resolution, which gives a reasonably good signal-to-noise ratio.

RESULTS AND DISCUSSION

Sorption. Figure 2 shows the kinetics of AZS sorption. The sorption of AZS on iron–montmorillonite and iron oxide was rapid, and the equilibrium was attained within 1.5 and 5 h, respectively. In the case of Fe-saturated humic acid the equilibrium time was 20 h. No degradation took place within these time intervals.

AZS sorption isotherms on the Fe^{3+}-saturated colloids showed different shapes, as shown in **Figure 3**.

The sorption isotherms on iron oxide and iron–humate were linear or of the C-type according to the classification of Giles et al. (*14*). This shape is characterized by a constant partitioning of solute between solution and adsorbing substrate. On the contrary, the isotherm on iron–clay was of the S-type, indicating that the sorption becomes increasingly favored as concentration rises and is usually ascribed to a strong competition with the solvent molecules for substrates sites. Sorption parameters K_{ads} and $1/n_{ads}$ were obtained by the fit of the sorption experimental data to the Freundlich equation (**Table 1**).

The values of Freundlich constants indicate that iron oxide shows the highest sorptive capacity toward AZS, followed by iron–clay and iron–humate, respectively. AZS is a weak acid with a pK_a value of 3.6 (*3*); therefore, it is prevalently in anionic form over the pH range studied. Among the colloids tested, only iron oxide surfaces are positively charged at the pH value of the suspension and are able to interact favorably with AZS anionic species. The zero point of charge (ZPC) of amorphous iron oxides occurs generally in the pH range of 7.5–9 (*15*). This could explain the high sorption level observed on iron oxide. On the other hand, the surface acidity of montmorillonite–iron-saturated may be responsible for the sorption measured on clay. The acidity of smectite clays is due to the polarizing power of exchange metal ions. Small highly charged exchange ions such as Fe^{3+} can polarize the coordinated water molecules, promoting the release of protons into the interlamellar zone, which becomes more acidic that the bulk suspension (*15*). Consequently, the AZS molecules near the clay surfaces can be in the undissociated form and can overcome the electrostatic repulsion. Also iron–humate shows a good affinity for AZS. Recent results of ours indicate that organic matter is important in AZS sorption only if the herbicide is at least partly in the neutral form (*4*). An examination of Freundlich constants for the sorption experiments on acid humic at different pH values supports this hypothesis (**Table 1**; **Figure 4**).

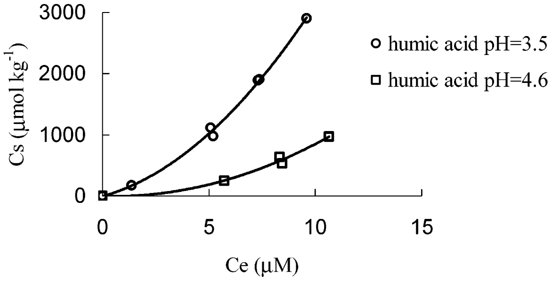

Figure 4. Sorption of azimsulfuron on humic acid at different pH values.

The affinity of humic acid for AZS is high at pH 3.5, but decreases drastically at pH 4.6. On the other hand, iron–humate at pH 4.6 is an adsorbent as strong as humic acid at pH 3.5. X-ray diffractometric and IR and EPR spectroscopic evidences on iron–humate clearly show that the Fe ion is octahedrally coordinated by the humic matter and its oxidation state is III (*16–18*). The binding of humic substances to ferric ions produces hydrophobic surfaces. In fact, iron–humates display their nonpolar group at the surface (*19*); therefore, they are markedly less soluble in water than the parent humic acids (*20*). The rearrangement that occurs upon iron binding may account for the long equilibrium time (20 h) observed in the AZS sorption on iron–humate compared with the other colloids. In fact, the hydrophobic surface of the metal–humate complex can shield the binding sites. The results suggest that, as AZS overcomes the hydrophobic screen, a strong interaction between herbicide and iron–humate takes place.

Degradation. With elapsing time, AZS degradation was observed in all systems investigated. **Figure 5** shows the amounts of AZS remaining in the different colloid suspensions.

Independent of the nature and pH of the colloid system, the metabolites ADP and MPS (**Figure 1**), arising from a hydrolytic cleavage of the sulfonylurea bridge, were the only byproducts observed. The hydrolysis followed simple pseudo-first-order kinetics (**Table 2**). Kinetic data were calculated using as C_0 (concentration of herbicide at $t = 0$) and t_0 (starting time of degradation) the concentration and equilibrium time of the sorption process, respectively.

Colloids play a catalytic role in the herbicide hydrolysis, the slowest degradation being observed in a colloid-free blank solution. Iron–humate is most effective in promoting AZS degradation, followed by iron oxide and iron–clay. The trend indicates that neither the pH value of the colloid suspensions nor the amount of adsorbed herbicide is a critical factor in AZS

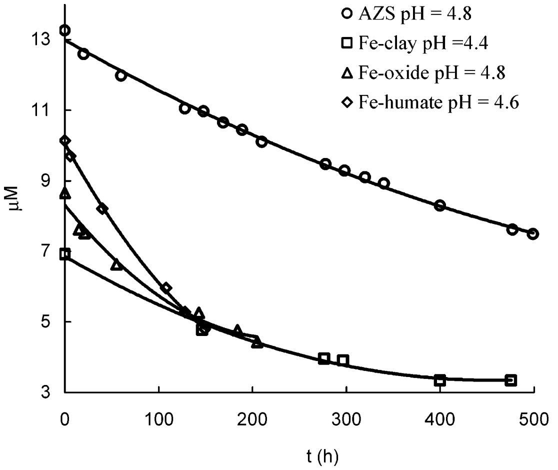

Figure 5. Disappearance of azimsulfuron with elapsing time in the colloidal systems investigated.

Table 2. Kinetic Data of Degradation of Azimsulfuron on Different Systems

system	pH[a]	$k_{obs} \times 10^{-3}$ (h^{-1})	$t_{1/2}$ (h)	r[b]
AZS	4.8	1.2	578	0.978
iron oxide	4.8	3.4	204	0.955
iron-clay	4.4	1.8	385	0.981
iron–humate	4.6	5.1	136	0.992

[a] pH of aqueous suspension. [b] Correlation coefficient.

degradation. In fact, the highest degradation extent was observed neither on iron−clay suspension, which is most acidic, nor on iron oxide, which is most effective in adsorption. Besides, the catalytic activity of iron oxide and iron−humate complex is 2−3 times higher compared with iron(III)−clay. This suggests that the interaction of AZS with iron−humate and iron oxide is different from that with iron−clay.

FT-IR Analyses. FT-IR spectroscopy is a useful tool to obtain information about the mechanisms of pesticide sorption on colloid surfaces (*7*, *12*, *21*). Because water competes with herbicide molecules for binding surfaces, it is rather difficult to acquire spectroscopic evidence from aqueous solutions. Therefore, FT-IR spectra were recorded on colloids treated with an AZS chloroform solution. The FT-IR spectra of AZS, in the free, protonated, and iron−clay complex forms, are compared in **Figure 6**.

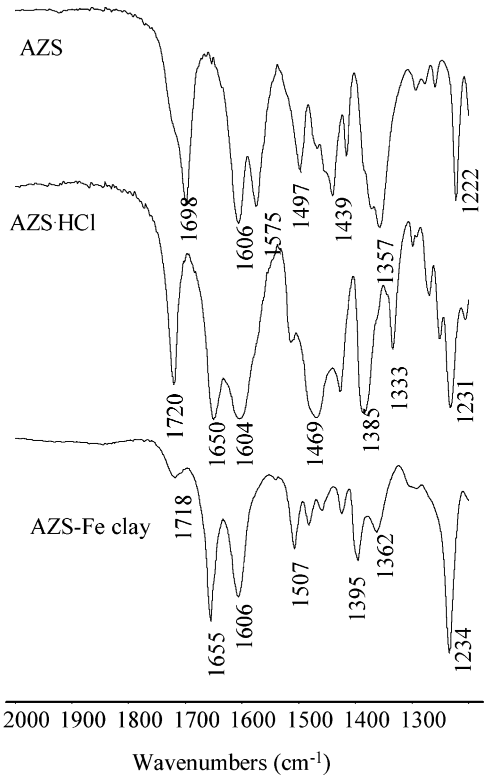

Figure 6. FT-IR spectra of azimsulfuron, azimsulfuron hydrochloride, and azimsulfuron–iron montmorillonite complex.

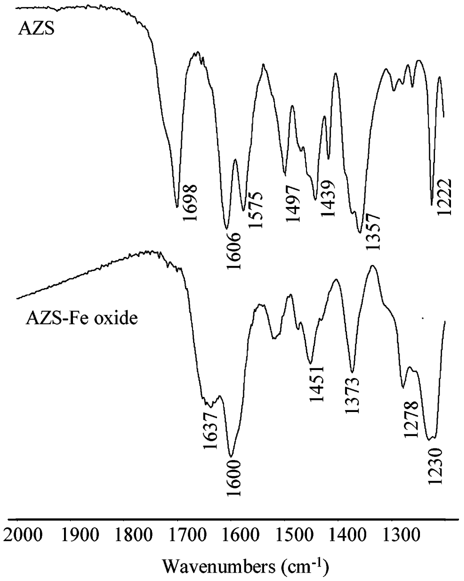

Figure 7. FT-IR spectra of azimsulfuron and its complex with iron oxide.

The spectra indicate that the herbicide undergoes significant changes upon interaction with montmorillonite. AZS exhibits an absorption at 1698 cm^{-1} due to the stretching mode of the carbonyl group, which shifts to 1718 cm^{-1} in the AZS iron−montmorillonite complex. The displacement to higher wavenumbers suggests an increase in the double-bond character of the C=O moiety, most likely due to an electron-withdrawing effect from a protonated neighboring group. Further distinguishing features of the AZS iron−montmorillonite complex are absorptions centered at 1507 and 1655 cm^{-1}, respectively, the latter value typical of protonated aromatic nitrogenous heterocycles (*22*, *23*). Most likely, the protonation takes place on one of the pyrimidine nitrogen atoms, which are the most basic sites in the molecule because of the strong electron-releasing effect of two OCH_3 groups of the pyrimidine ring. The proton sources are probably the acidic water molecules surrounding the iron ions. These findings agree with the spectrum of AZS hydrochloride (**Figure 6**) that shows bands similar to those observed for the AZS iron−montmorillonite complex. For instance, the absorptions at 1718 and 1655 cm^{-1} of the clay complex correspond well to those at 1720 and 1650 cm^{-1} for protonated AZS.

The IR spectrum of the AZS−iron oxide complex does not show absorptions attributable to protonated AZS (**Figure 7**).

In the IR spectrum of the iron oxide complex the asymmetric vibrations due to carbonyl and sulfonyl groups of AZS at 1698 and 1357 cm^{-1} in the free form are shifted to 1637 and 1278 cm^{-1}, respectively. The downward displacement suggests a decrease of double-bond character of both carbonyl and sulfonyl groups. This could indicate Fe^{3+} coordination to the AZS sulfononylurea group acting as a bidentate bridging ligand through sulfonyl and carbonyl oxygen atoms. This binding mode, giving rise to a six-membered chelated ring, explains the peculiar IR features of the AZS−iron oxide complex. In fact, metal coordination to the sulfonamide group shifts the SO_2 stretches, particularly the asymmetric one, to lower wavenumbers, owing to the electron-withdrawing effect of metal coordination (*12*, *24*).

It was not possible to perform a FT-IR study of the AZS−iron humate complex because the intense absorption bands due to the humic moiety mask those due to the herbicide.

Effect of Oxalic Acid on Iron−Humate Sorption. To obtain spectroscopic information about the binding mode of AZS to iron−humate, a further sorption experiment was performed. An iron−humate sample (20 mg) was added to a solution containing equimolar amounts of AZS and oxalic acid (12.7 μM), which is a strong ligand for Fe(III) ions (*25*). After equilibration (20 h), the suspension (pH 4.8) was tested for AZS. The presence of oxalic acid decreased drastically the amount of adsorbed AZS (∼75%), indicating that oxalic acid competes with AZS for the binding sites on iron−humate. This feature may be ascribed to a greater tendency of oxalic acid compared with AZS to form complexes with ferric ions. Therefore, it is plausible that also the interaction between AZS and iron−humate can occur via a metal coordination, even if actually we cannot assign the AZS donor groups coordinated to Fe ions.

Conclusions. The sorption mechanisms of AZS on Fe^{3+}-rich soil colloids depend on the type of colloid. According to FT-IR spectra, the sorption of AZS on iron−clay involves the protonation of one of the two basic nitrogen atoms of the pyrimidine ring of the herbicide due to the acidic water surrounding Fe^{3+}-saturating ions. On the other hand, the formation of a six-membered chelated complex, involving carbonyl and sulfonyl oxygen atoms, promotes AZS adsorption on iron oxide.

The different sorption mechanisms affect the degradation rate of AZS. The hydrolysis is much faster when the herbicide interacts with colloids by formation of coordination bonds, as in the case of iron oxide. The complexation of iron by oxygen atoms of the sulfonylurea bridge weakens the sulfonamidic C−N bond and facilitates its hydrolytic cleavage from water. Most probably, a similar mechanism acts also in the case of iron−humate.

In the presence of iron−clay, the lower pH of the suspension affords the protonation of the pyrimidine ring and draws electron density away from the sulfonylurea bridge. This electronic effect is less important than a chelation process in weakening the C−N bond and slows the AZS degradation.

In conclusion, the results indicate that the distribution of Fe^{3+} ions among organic and inorganic colloids can affect differently the sorption and degradation of AZS herbicide.

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